

# CANONICAL QUANTUM OBSERVABLES FOR MOLECULAR SYSTEMS APPROXIMATED BY AB INITIO MOLECULAR DYNAMICS

AKU KAMMONEN, MATTIAS SANDBERG, AND ANDERS SZEPESSY

**ABSTRACT.** Ab initio molecular dynamics based on the electron ground state eigenvalue can be used to approximate quantum observables in the canonical ensemble when the temperature is low compared to the first electron eigenvalue gap. This work proves that a certain weighted average of the different ab initio dynamics, corresponding to each electron eigenvalue, approximates quantum observables for all temperatures. The proof uses the semi-classical Weyl law to show that canonical quantum observables of nuclei-electron systems, based on matrix valued Hamiltonian symbols, can be approximated by ab initio molecular dynamics with the error proportional to the electron-nuclei mass ratio. The result includes observables that depend on correlations in time. A combination of the Hilbert-Schmidt inner product for quantum operators and Weyl's law shows that the error estimate holds for observable and Hamiltonian symbols that have three and five bounded derivatives, respectively, provided the electron eigenvalues are distinct for any nuclei position.

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## 1. MOTIVATION FOR THIS WORK

It is well known that quantum observables in the canonical ensemble in some situations can be approximated by molecular dynamics simulations with constant number of particles, volume and temperature, see [9]. The first mathematical result of such a semi-classical limit was by Wigner [12]: Wigner introduced the "Wigner"-function, based on solutions to the Schrödinger equation with scalar potentials, and made an expansion in the Planck constant to relate the canonical quantum observable, as defined by von Neumann [11], to the classical Gibbs phase-space average.

In this work we study molecular dynamics approximations of canonical ensemble averages for quantum observables in the case of Hamiltonians consisting of the kinetic energy of nuclei and a matrix valued potential for nuclei-electron interaction and electron kinetic energy. The purpose of having a matrix valued operator for the electron part in the Hamiltonian is to replace the time evolution for the electrons by the Schrödinger electron eigenvalue problem. An advantage with including the electron part as a matrix valued operator is that the classical limit, as the nuclei-electron mass ratio tends to infinity, can be derived as we will explain. This classical limit can then be approximated by ab initio molecular dynamics simulations for nuclei, with the potential generated by the electron eigenvalue problem, see [9] and [8], which requires less computational effort than to solve the Schrödinger equation with time dependent electrons. If the temperature is very small in comparison with the minimal difference of the second and first eigenvalue of the electron potential, the probability for the quantum system to be in excited electron states is negligible and canonical ab initio molecular dynamics based on the ground state electron eigenvalue yields accurate approximations. When the temperature is not small compared to this electron eigenvalue gap, the probability to be in excited states is substantial. An important question, which seems mathematically open, is: How to modify the canonical ab initio molecular dynamics to accurately approximate quantum observables, based on matrix valued potentials and all temperatures?

The aim here is to derive molecular dynamics methods that accurately, in mathematical sense, approximate the quantum observable also in the case where the temperature can be large compared to this first spectral gap. The approximation consists of a weighted sum, over electron eigenvalues, of molecular dynamics observables based on the corresponding scalar Hamiltonians, which are equal to the eigenvalues of the original matrix valued Hamiltonian symbol. Also the weights, which are the probabilities to be in the corresponding electron states, are determined precisely as molecular dynamics observables.

Sections 2 and 3 present analysis with quantum observables not depending on correlations in time and observables depending on time correlations, respectively. The main result is that canonical quantum observables, based on Schrödinger Hamiltonians with matrix valued potentials, can for any positive temperature be approximated by ab initio molecular dynamics: the approximation error is bounded by the electron-nuclei mass ratio,  $M^{-1/2}$ , times a constant, provided the observable symbols have up to three derivatives bounded in  $L^2(\mathbb{R}^{2N})$ , the Hamiltonian symbol has five derivatives and the electron eigenvalues are distinct for any nuclei position. An improved approximation error  $\mathcal{O}(M^{-1})$  holds with additional assumptions. The result includes observables that depend on correlations in time. The main mathematical tool is the semi-classical Weyl law, as formulated e.g. in [13] and [10].

The semi-classical Weyl law has been used before in [10] to approximate canonical quantum observables, based on matrix valued potentials, by phase-space averages. A difference is that our error estimates are not based on the Calderon-Vaillancourt theorem

that bounds the  $L^2$  operator norm of a symbol by  $L^\infty$  estimates of derivatives of order  $N$  of the symbol. Instead we use a combination of the Hilbert-Schmidt norm of quantum observables and Weyl's law to obtain bounds in terms of the  $L^2(\mathbb{R}^{2N})$  norm of remainder symbols based on three and five derivatives of the observables and the Hamiltonian, respectively. Other differences are in the use of projections to electron states, that here is based on a nonlinear eigenvalue problem solved by Cauchy-Kovalevsky's theorem, and that we analyze the weights to be in the different electron states and determine them as molecular dynamics observables.

## 2. THE SCHRÖDINGER EQUATION AND GIBBS ENSEMBLES

Let  $\Phi_n : \mathbb{R}^N \rightarrow \mathbb{C}^d$  for  $n = 1, 2, 3, \dots$  be the infinite sequence of all normalized  $[L^2(\mathbb{R}^N)]^d$  eigenfunctions, with the corresponding eigenvalues  $E_n \in \mathbb{R}$ , of the Schrödinger operator

$$\hat{H} = -\frac{1}{2M} \mathbf{I} \Delta + V(x),$$

i.e.

$$(2.1) \quad \hat{H} \Phi_n = E_n \Phi_n,$$

where  $V : \mathbb{R}^N \rightarrow \mathbb{C}^{d^2}$  is a Hermitian matrix valued confining potential and  $\mathbf{I} \Delta$  is the  $d \times d$  identity matrix times the Laplacian in  $\mathbb{R}^N$ , modeling the nuclei kinetic energy. Hence, the quantum model consists of nuclei coordinates that are in  $\mathbb{R}^N$  and the wave functions  $\Phi_n$  can take  $d$  discrete values, based on a discretization of the electron eigenvalue problem with a corresponding discrete Hamiltonian given by the matrix  $V(x)$ , for each nuclei configuration  $x$ . Here  $M$  is the nuclei-electron mass ratio, which is assumed to be a number much larger than one. The setting with individual nuclei masses and a diagonal mass matrix  $M$  can be transformed to the form (2.1) by introducing the new coordinates  $M_1^{1/2} \bar{x} = M^{1/2} x$ , which transforms the Hamiltonian into  $-(2M_1)^{-1} \mathbf{I} \Delta_{\bar{x}} + V(M_1^{1/2} M^{-1/2} \bar{x})$ . To handle the spectrum of  $\hat{H}$  we assume that the smallest eigenvalue  $\lambda_1(x)$  of  $V(x)$  tends to infinity as  $|x| \rightarrow \infty$ . This assumption implies that the spectrum of  $\hat{H}$  is discrete, see [2]. Therefore the set of eigenfunctions  $\{\Phi_n\}_{n=1}^\infty$  forms a complete  $L^2(\mathbb{R}^N, \mathbb{C}^d) = [L^2(\mathbb{R}^N)]^d$  basis. To have a complete set of eigenfunctions in  $[L^2(\mathbb{R}^N)]^d$  is crucial for the analysis of the canonical quantum ensemble average in this work, which is based on the concept of the trace of quantum operators introduced by von Neumann [11].

We will use the scalar product

$$\langle v, w \rangle := \int_{\mathbb{R}^N} \underbrace{v^*(x) \cdot w(x)}_{\sum_{j=1}^d v_j^*(x) w_j(x)} dx,$$

to evaluate observables for  $v, w \in [L^2(\mathbb{R}^N)]^d$ . Consider the Weyl quantized operator  $\hat{A}$  that maps  $[L^2(\mathbb{R}^N)]^d$  to  $[L^2(\mathbb{R}^N)]^d$  and is defined from a  $d \times d$  matrix valued symbol  $A : \mathbb{R}^{2N} \rightarrow \mathbb{C}^{d^2}$  in the Schwartz class by

$$\hat{A} \Phi(x) = \left( \frac{\sqrt{M}}{2\pi} \right)^N \int_{\mathbb{R}^N} \int_{\mathbb{R}^N} e^{iM^{1/2}(x-y) \cdot p} A\left(\frac{x+y}{2}, p\right) \Phi(y) dp dy.$$

For instance, the symbol  $H(x, p) := \frac{|p|^2}{2} \mathbf{I} + V(x)$  yields  $\hat{H} = -(2M)^{-1} \mathbf{I} \Delta + V(x)$ . This definition implies that  $\hat{A}$  has the integral kernel  $K_A(x, y)$

$$\hat{A} \Phi(x) = \int_{\mathbb{R}^N} K_A(x, y) \Phi(y) dy$$

where

$$K_A(x, y) = \left(\frac{\sqrt{M}}{2\pi}\right)^N \int_{\mathbb{R}^N} e^{iM^{1/2}(x-y) \cdot p} A\left(\frac{x+y}{2}, p\right) dp.$$

Further properties and background on the Weyl quantization is presented e.g. in [13]. The principal idea in this work is to view such kernels as infinite dimensional matrices and determine their trace as operators on  $[L^2(\mathbb{R}^N)]^d$ . The  $[L^2(\mathbb{R}^N)]^d$  trace is a composition of the trace in  $L^2(\mathbb{R}^N)$  and the trace of  $d \times d$  matrices: integrate over all  $x$  in  $\mathbb{R}^N$  and for each  $x$  sum the diagonal elements in the  $d \times d$  matrix. That is, the  $L^2$  measure for the trace is the product measure composed of the Lebesgue measure on  $\mathbb{R}^N$  times the counting measure on  $\mathbb{C}^d$ . The analysis here uses the fact that the  $[L^2(\mathbb{R}^N)]^d$  trace of a Weyl operator based on a  $d \times d$  matrix valued symbol is equal to the phase-space average of its symbol trace, since we have

$$\begin{aligned} \sum_{n=1}^{\infty} \langle \Phi_n, \hat{A} \Phi_n \rangle &= \text{trace } \hat{A} \\ (2.2) \quad &= \int_{\mathbb{R}^N} \text{trace } K_A(x, x) dx \\ &= \left(\frac{\sqrt{M}}{2\pi}\right)^N \int_{\mathbb{R}^N} \int_{\mathbb{R}^N} \text{trace } A(x, p) dp dx, \end{aligned}$$

where

$$\text{trace } A(z) = \sum_{j=1}^d A_{jj}(z)$$

with the coordinate  $z = (x, p) \in \mathbb{R}^{2N}$  in phase-space and its Lebesgue measure  $dz = dx dp$ . In fact also the composition of two Weyl operators is determined by the phase-space average as follows.

**Lemma 2.1.** *The composition of two Weyl operators satisfies*

$$\text{trace}(\hat{A}\hat{B}) = \left(\frac{M^{1/2}}{2\pi}\right)^N \int_{\mathbb{R}^{2N}} \text{trace}(A(z)B(z)) dz,$$

where  $A(z)B(z)$  is the matrix product of the two  $d \times d$  matrices  $A(z)$  and  $B(z)$ .

This result is known, see [10]. We include a proof since it is important for the work here.

*Proof.* The kernel of the composition is

$$K_{AB}(x, y) = \left(\frac{M^{1/2}}{2\pi}\right)^{2N} \int_{\mathbb{R}^{3N}} A\left(\frac{x+x'}{2}, p\right) B\left(\frac{x'+y}{2}, p'\right) e^{iM^{1/2}((x-x') \cdot p + (x'-y) \cdot p')} dp' dp dx'$$

so that the trace of the composition becomes

$$\begin{aligned} &\text{trace}(\hat{A}\hat{B}) \\ &= \int_{\mathbb{R}^N} \text{trace } K_{AB}(x, x) dx \\ &= \left(\frac{M^{1/2}}{2\pi}\right)^{2N} \int_{\mathbb{R}^{4N}} \text{trace}\left(A\left(\frac{x+x'}{2}, p\right) B\left(\frac{x'+x}{2}, p'\right)\right) e^{iM^{1/2}((x-x') \cdot p + (x'-x) \cdot p')} dp' dp dx' dx \\ &= \left(\frac{M^{1/2}}{2\pi}\right)^{2N} \int_{\mathbb{R}^{4N}} \text{trace}(A(y, p) B(y, p')) e^{iM^{1/2}y' \cdot (p-p')} dp' dp dy' dy \\ &= \left(\frac{M^{1/2}}{2\pi}\right)^N \int_{\mathbb{R}^{2N}} \text{trace}(A(y, p) B(y, p)) dp dy, \end{aligned}$$

using the change of variables  $(y, y') = ((x + x')/2, x - x')$ , which verifies the claim.  $\square$

The aim here is to find molecular dynamics approximations to the Gibbs canonical quantum ensemble average, defined as

$$\sum_{n=1}^{\infty} \langle \Phi_n, \hat{A} \Phi_n \rangle e^{-E_n/T} = \sum_{n=1}^{\infty} \langle \Phi_n, e^{-\hat{H}/T} \hat{A} \Phi_n \rangle$$

for a positive temperature  $T$  and an observable symbol  $A : \mathbb{R}^{2N} \rightarrow \mathbb{C}^{d^2}$ . In Section 3 we consider related time dependent observables. The trace property of Lemma 2.1 shows that an approximation of the Gibbs observable, where the order of the operations of exponentiation and quantization have been reversed, satisfies

$$\begin{aligned} \sum_{n=1}^{\infty} \langle \Phi_n, \widehat{e^{-H/T} \hat{A}} \Phi_n \rangle &= \text{trace}(\widehat{e^{-H/T} \hat{A}}) \\ &= \left(\frac{M^{1/2}}{2\pi}\right)^N \int_{\mathbb{R}^N} \text{trace}(A(z) e^{-H(z)/T}) dz \end{aligned}$$

and in normalized form

$$(2.3) \quad G := \frac{\text{trace}(\widehat{e^{-H/T} \hat{A}})}{\text{trace}(\widehat{e^{-H/T}})} = \frac{\int_{\mathbb{R}^{2N}} \text{trace}(A(z) e^{-H(z)/T}) dz}{\int_{\mathbb{R}^{2N}} \text{trace}(e^{-H(z)/T}) dz}.$$

We first consider symbols for observables that can be diagonalized by the same transformation as the Hamiltonian, which for instance includes the scalar observables. More precisely let  $\tilde{A} : \mathbb{R}^{2N} \rightarrow \mathbb{C}^{d^2}$  be a symbol in the Schwartz class and consider symbols in the matrix product form  $A(z) = \tilde{\Psi}(x) \tilde{A}(z) \tilde{\Psi}^*(x)$ , where  $\tilde{\Psi}(x)$  is the  $d \times d$  matrix composed of the eigenvectors to  $V(x)$  as columns, i.e.

$$(2.4) \quad \sum_{j=1}^d V_{ij}(x) \tilde{\Psi}_{jk}(x) = \tilde{\lambda}_k(x) \tilde{\Psi}_{ik}(x),$$

and  $\tilde{\lambda}_k(x), k = 1, \dots, d$ , denote the eigenvalues of  $V(x)$  in increasing order. Here  $\tilde{\Psi}^*(x)$  is the Hermitian adjoint of  $\tilde{\Psi}(x)$  in  $\mathbb{C}^d$ . Then  $\tilde{\Psi}(x)$  diagonalizes  $H(z)$  and it and  $A(z)$  satisfy:

$$(2.5) \quad \begin{aligned} H(z) &= \tilde{\Psi}(x) \tilde{H}(z) \tilde{\Psi}^*(x), & \text{where } \tilde{H}_{jk}(z) &= \delta_{jk} \left( \frac{|p|^2}{2} + \tilde{\lambda}_j(x) \right), \\ A(z) &= \tilde{\Psi}(x) \tilde{A}(z) \tilde{\Psi}^*(x), & \text{where } \tilde{A}(z) &= \tilde{\Psi}^*(x) A(z) \tilde{\Psi}(x). \end{aligned}$$

The diagonal property of  $e^{-\tilde{H}/T}$  shows that the trace satisfies

$$\begin{aligned} \text{trace}(A(z) e^{-H(z)/T}) &= \text{trace}(\tilde{A}(z) e^{-\tilde{H}(z)/T}) \\ &= \sum_{j=1}^d \tilde{A}_{jj}(z) e^{-\tilde{H}_{jj}(z)/T}. \end{aligned}$$

We obtain by (2.3) the approximate Gibbs quantum observable as a sum

$$G = \frac{\sum_{j=1}^d \int_{\mathbb{R}^{2N}} \tilde{A}_{jj}(z) e^{-\tilde{H}_{jj}(z)/T} dz}{\sum_{j=1}^d \int_{\mathbb{R}^{2N}} e^{-\tilde{H}_{jj}(z)/T} dz}$$

and each term can be written in canonical ensemble form:

**Lemma 2.2.** *The approximate canonical ensemble average satisfies, for  $T > 0$ ,*

$$(2.6) \quad \frac{\text{trace}(\widehat{e^{-H/T}} \hat{A})}{\text{trace}(\widehat{e^{-H/T}})} = \sum_{j=1}^d q_j \int_{\mathbb{R}^{2N}} \tilde{A}_{jj}(z) \frac{e^{-\tilde{H}_{jj}(z)/T} dz}{\int_{\mathbb{R}^{2N}} e^{-\tilde{H}_{jj}(z')/T} dz'}$$

based on the probabilities

$$q_j := \frac{\int_{\mathbb{R}^{2N}} e^{-\tilde{H}_{jj}(z)/T} dz}{\sum_{k=1}^d \int_{\mathbb{R}^{2N}} e^{-\tilde{H}_{kk}(z')/T} dz'}, \quad j = 1, \dots, d$$

to be in state  $j$ .

In Section 3 we analyze the trace based on the time independent Gibbs density operator  $e^{-\hat{H}/T}$ , using instead the transformation  $\hat{A} = \hat{\Psi} \hat{\tilde{A}} \hat{\Psi}^*$  for a diagonal symbol  $\tilde{A} : [0, \infty) \times \mathbb{R}^{2N} \rightarrow \mathbb{C}^{d^2}$  with an orthogonal matrix  $\Psi : \mathbb{R}^N \rightarrow \mathbb{C}^{d^2}$  diagonalizing a non linear perturbed eigenvalue problem. We will use the composition rule

$$A \# B(x, p) := e^{\frac{i}{2M^{1/2}}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} A(x, p) B(x', p') \Big|_{(x,p)=(x',p')},$$

$$\hat{A} \hat{B} = \widehat{A \# B}$$

see [13], to determine the symbol for compositions of Weyl operators. Expansion of the exponential in the composition rule leads to the so called Moyal expansion. The usual estimates of remainder terms in Moyal expansions determine the  $L^2(\mathbb{R}^N)$  operator norm from  $L^\infty$  norm estimates of derivatives of order  $N$  of the remainder symbol, using the Calderon-Vaillancourt theorem, see Theorem 4.23 in [13]. To avoid derivatives of high order, if  $N$  is large, we instead estimate the remainder terms in the form  $\text{trace}(\hat{R} \hat{C})$ , for Hermitian operators  $\hat{R}$  and  $\hat{C}$  on  $L^2(\mathbb{R}^N)$ , by the  $L^2$  norms of their symbols, using the Hilbert-Schmidt inner product,  $\text{trace}(\hat{R}^* \hat{C})$ , the Hilbert-Schmidt norm,  $\|\hat{R}\|_{\mathcal{HS}}^2 = \text{trace}(\hat{R}^* \hat{R}) = \text{trace}((\hat{R})^2)$ , and Lemma 2.1 as follows

$$(2.7) \quad \begin{aligned} |\text{trace}(\hat{R}^* \hat{C})|^2 &\leq \text{trace}(\hat{R}^* \hat{R}) \text{trace}(\hat{C}^* \hat{C}) \\ &= \left(\frac{M^{1/2}}{2\pi}\right)^{2N} \int_{\mathbb{R}^{2N}} \text{trace } R^2(z) dz \int_{\mathbb{R}^{2N}} \text{trace } C^2(z) dz. \end{aligned}$$

Lemmas 3.2 and 3.3 estimates the  $L^2(\mathbb{R}^{2N})$  norm of remainder terms in Weyl compositions by integration by parts, roughly as follows

$$(2.8) \quad \begin{aligned} &\int_{\mathbb{R}^{2N}} \left| e^{\frac{i}{2M^{1/2}}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} \underbrace{A(x, p) B(x', p')}_{=: r(x, p, x', p')} \right|_{z'=z}^2 dz \\ &= \int_{\mathbb{R}^{4N}} \left( e^{\frac{i}{2M^{1/2}}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} r(z, z') \right)^* e^{\frac{i}{2M^{1/2}}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} r(z, z') \delta(z - z') dz dz' \\ &= \int_{\mathbb{R}^{4N}} r^*(z, z') e^{\frac{-i}{2M^{1/2}}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} \left( e^{\frac{i}{2M^{1/2}}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} r(z, z') \delta(z - z') \right) dz dz' \\ &= \dots \leq \frac{1}{(2\pi)^{4N}} \|\mathcal{F}A\|_{L^1(\mathbb{R}^{2N})}^2 \|B\|_{L^2(\mathbb{R}^{2N})}^2, \end{aligned}$$

where " $= \dots \leq$ " is explained in the proof using the Fourier transform of the Dirac measure  $\delta(z - z')$ , that  $i\nabla_x \cdot \nabla_p$  is anti-Hermitian, so that  $(e^{\frac{i}{2M^{1/2}}\nabla_x \cdot \nabla_p})^* = e^{-\frac{i}{2M^{1/2}}\nabla_x \cdot \nabla_p}$  is unitary, and applying Young's inequality to convolutions of Fourier transforms. In our proof of Theorems 3.6 and 3.7 and to prove (3.48) in Theorem 3.5 we need this estimate only in the special case where one function depends only on the  $x$ -coordinate, i.e.  $A(x)$ , and then the right hand side instead becomes  $\|A\|_{L^\infty(\mathbb{R}^N)}^2 \|B\|_{L^2(\mathbb{R}^{2N})}^2$ .

**Remark 2.3.** A method to handle projections to electron states is to normalize with respect to that state and use

$$\frac{\sum_{n=1}^{\infty} \langle \Phi_n, \widehat{\Psi_j \tilde{A}_{jj} \Psi_j^*} e^{-H/T} \Phi_n \rangle}{\sum_{n=1}^{\infty} \langle \Phi_n, \widehat{\Psi_j \Psi_j^*} e^{-H/T} \Phi_n \rangle} = \int_{\mathbb{R}^{2N}} \tilde{A}_{jj}(z) \frac{e^{-\tilde{H}_{jj}(z)/T}}{\int_{\mathbb{R}^{2N}} e^{-\tilde{H}_{jj}(\bar{z})/T} d\bar{z}} dz.$$

□

The canonical phase space ensemble averages of  $\tilde{A}_{jj}$  and the weight  $q_j$  in (2.6) can be determined by molecular dynamics as follows. The molecular dynamics observable

$$A_j := \int_{\mathbb{R}^{2N}} \tilde{A}_{jj}(z) \frac{e^{-\tilde{H}_{jj}(z)/T}}{\int_{\mathbb{R}^{2N}} e^{-\tilde{H}_{jj}(z')/T} dz'} dz$$

can by ergodicity be computed by the time average

$$A_j = \lim_{\tau_* \rightarrow \infty} \tau_*^{-1} \int_0^{\tau_*} \tilde{A}_{jj}(z_t) dt,$$

where  $z_t$  solves the Langevin equation

$$(2.9) \quad \begin{aligned} dx_t &= p_t dt \\ dp_t &= -\nabla \tilde{\lambda}_j(x_t) dt - \alpha p_t dt + \sqrt{2\alpha T} dW_t. \end{aligned}$$

Here  $W : [0, \infty) \rightarrow \mathbb{R}^N$  is the  $N$  dimensional standard Wiener process and  $\alpha$  is a positive constant. If each eigenvalue  $\lambda_j(x)$  is smooth and similar to  $|x|^\gamma$  as  $|x| \rightarrow \infty$ , for some  $\gamma > 1$ , Theorem 0.1 in [6] shows that the corresponding Langevin dynamics is ergodic with an exponential trend to the equilibrium.

The probabilities  $q_j$  can also be determined from molecular dynamics in the ground state canonical ensemble by

$$q_j = \frac{\bar{q}_j}{\sum_{k=1}^d \bar{q}_k}$$

where

$$\bar{q}_j := \frac{\int_{\mathbb{R}^N} e^{-(\tilde{\lambda}_j(x) - \tilde{\lambda}_1(x))/T} e^{-\tilde{\lambda}_1(x)/T} dx}{\int_{\mathbb{R}^N} e^{-\tilde{\lambda}_1(x)/T} dx}$$

and if  $z_t = (x_t, p_t)$  solves (2.9) with  $j = 1$  (i.e. the ground state), we have

$$\bar{q}_j = \lim_{\tau_* \rightarrow \infty} \tau_*^{-1} \int_0^{\tau_*} e^{-(\tilde{\lambda}_j(x_t) - \tilde{\lambda}_1(x_t))/T} dt.$$

Based on finite time,  $\tau_*$ , molecular dynamics, the approximation error for the observable  $G$  becomes  $\mathcal{O}(e^{-c\alpha\tau_*})$  for a positive constant  $c$ , see Theorem 0.1 in [6]. In the case of observables depending on correlation in time there are additional error terms as we will see in Section 3.

**Remark 2.4.** In the case that all observable components are the same, i.e.  $\tilde{A}_{jj} = \tilde{A}_{11}$  for  $j = 1, \dots, d$ , the approximate canonical ensemble average can be determined by one molecular dynamics path as follows. Let the potential  $\check{\lambda} : \mathbb{R}^N \rightarrow \mathbb{R}$  be defined by

$$\check{\lambda}(x) := -T \log \left( \sum_{j=1}^d e^{-\tilde{\lambda}_j(x)/T} \right)$$

so that

$$e^{-\check{\lambda}(x)/T} = \sum_{j=1}^d e^{-\tilde{\lambda}_j(x)/T}.$$

Then we have

$$\frac{\sum_{j=1}^d e^{-\tilde{H}_{jj}(x,p)}}{\int_{\mathbb{R}^{2N}} \sum_{j=1}^d e^{-\tilde{H}_{jj}(z)} dz} = \frac{e^{-(|p|^2/2 + \check{\lambda}(x))/T}}{\int_{\mathbb{R}^{2N}} e^{-(|p|^2 + \check{\lambda}(x))/T} dx dp},$$

which implies

$$\begin{aligned} \frac{\text{trace}(A \widehat{e^{-H/T}})}{\text{trace}(\widehat{e^{-H/T}})} &= \frac{\int_{\mathbb{R}^{2N}} \sum_{j=1}^d \tilde{A}_{jj}(z) e^{-\tilde{H}_{jj}(z)/T} dz}{\int_{\mathbb{R}^{2N}} \sum_{j=1}^d e^{-\tilde{H}_{jj}(z)/T} dz} \\ &= \frac{\int_{\mathbb{R}^{2N}} \tilde{A}_{11}(z) \sum_{j=1}^d e^{-\tilde{H}_{jj}(z)/T} dz}{\int_{\mathbb{R}^{2N}} \sum_{j=1}^d e^{-\tilde{H}_{jj}(z)/T} dz} \\ &= \frac{\int_{\mathbb{R}^{2N}} \tilde{A}_{11}(x,p) e^{-(|p|^2/2 + \check{\lambda}(x))/T} dx dp}{\int_{\mathbb{R}^{2N}} e^{-(|p|^2 + \check{\lambda}(x))/T} dx dp}. \end{aligned}$$

By also defining the single Langevin path

$$\begin{aligned} \dot{x}_t &= p_t \\ \dot{p}_t &= -\nabla \check{\lambda}(x_t) - \alpha p_t + \sqrt{2\alpha T} \dot{W}_t, \end{aligned}$$

which has the invariant measure  $\frac{e^{-(|p|^2/2 + \check{\lambda}(x))/T} dx dp}{\int_{\mathbb{R}^{2N}} e^{-(|p|^2 + \check{\lambda}(x))/T} dx dp}$  for any positive  $\alpha$ , we obtain

$$\frac{\text{trace}(A \widehat{e^{-H/T}})}{\text{trace}(\widehat{e^{-H/T}})} = \lim_{\tau_* \rightarrow \infty} \tau_*^{-1} \int_0^{\tau_*} \tilde{A}_{11}(x_t, p_t) dt.$$

In the next section we study quantum effects and Theorem 3.5 proves an estimate for the canonical ensemble, based on  $e^{-\hat{H}/T}$ , including also time correlations.

### 3. TIME CORRELATED OBSERVABLES

In this section we study canonical quantum observables for correlations in time, namely

$$\text{trace}(\hat{A}_\tau \hat{B}_0 e^{-\hat{H}/T}) = \sum_{n=1}^{\infty} \langle \Phi_n, \hat{A}_\tau \hat{B}_0 e^{-\hat{H}/T} \Phi_n \rangle,$$

and the related variant  $\text{trace}(\hat{A}_\tau (\hat{B}_0 e^{-\hat{H}/T} + e^{-\hat{H}/T} \hat{B}_0))$ , based on the time dependent operator  $\hat{A}_\tau$ , which for  $\tau \in \mathbb{R}$  is defined by

$$(3.1) \quad \hat{A}_\tau := e^{i\tau M^{1/2} \hat{H}} \hat{A}_0 e^{-i\tau M^{1/2} \hat{H}},$$

with a matrix valued symbol  $A_0 : \mathbb{R}^{2N} \rightarrow \mathbb{C}^{d^2}$  in the Schwartz class. For instance the observable for the diffusion constant

$$\frac{1}{6\tau} \frac{3}{N} \sum_{k=1}^{N/3} |x_k(\tau) - x_k(0)|^2 = \frac{1}{2N\tau} (|x(\tau)|^2 + |x(0)|^2 - 2x(\tau) \cdot x(0))$$

uses the time-correlation  $\hat{x}(\tau) \cdot \hat{x}(0)$  where  $\hat{A}_\tau = \hat{x}_\tau \mathbf{I}$  and  $\hat{B}_0 = \hat{x}_0 \mathbf{I}$  and

$$\hat{x}_\tau \cdot \hat{x}_0 = \sum_{n=1}^N \sum_{j=1}^3 e^{i\tau M^{1/2} \hat{H}} \hat{x}_{n_j} e^{-i\tau M^{1/2} \hat{H}} \hat{x}_{n_j}.$$

To analyze the time evolution of  $\hat{A}_\tau$  we use transformed variables: assume that  $\Psi : \mathbb{R}^N \rightarrow \mathbb{C}^{d^2}$  and  $\Psi(x)$  is an orthogonal matrix with the Hermitian transpose  $\Psi^*(x)$  and define  $\bar{A} : [0, \infty) \times \mathbb{R}^{2N} \rightarrow \mathbb{C}^{d^2}$  by

$$(3.2) \quad \widehat{\bar{A}(\tau, z)} = \hat{\Psi}^*(x) \hat{A}_\tau \hat{\Psi}(x), \quad \tau \geq 0.$$



The matrix  $\Psi(x)$  we will use is defined precisely below and it approximates the matrix  $\tilde{\Psi}(x)$  that diagonalizes the potential matrix  $V(x)$  in the sense that  $\|\Psi(x) - \tilde{\Psi}(x)\| = \mathcal{O}(M^{-1})$ . We also assume that

$$\hat{B}_0 = \hat{\Psi} \widehat{\hat{B}_0} \hat{\Psi}^*,$$

and we restrict our study to the case where the  $d \times d$  matrix symbol  $\bar{A}(0, \cdot) = \bar{A}_0$  is diagonal. Let  $\alpha$  be any complex number and define the exponential

$$\hat{y}_t := \hat{\Psi}^* e^{t\alpha \hat{H}} \hat{\Psi}.$$

Differentiation shows that

$$(3.3) \quad \partial_t \hat{y}_t = \alpha \hat{\Psi}^* \hat{H} \hat{\Psi} \hat{\Psi}^* e^{t\alpha \hat{H}} \hat{\Psi} = \alpha \hat{\Psi}^* \hat{H} \hat{\Psi} \hat{y}_t$$

and we conclude that

$$(3.4) \quad \hat{y}_t = e^{t\alpha \hat{\Psi}^* \hat{H} \hat{\Psi}}.$$

The composition rule

$$(3.5) \quad A \# B(x, p) := e^{\frac{i}{2M^{1/2}}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} A(x, p) B(x', p') \Big|_{(x, p) = (x', p')},$$

$$\hat{A} \hat{B} = \widehat{A \# B}$$

see [13], implies

$$\hat{\Psi}^* \hat{H} \hat{\Psi} = (\Psi^* \# H \# \Psi)^\wedge$$

and we have

**Lemma 3.1.** *There holds*

$$\Psi^* \# H \# \Psi(x, p) = \Psi^*(x) H(x, p) \Psi(x) + \frac{1}{4M} \nabla \Psi^*(x) \cdot \nabla \Psi(x).$$

*Proof.* The composition in (3.5) shows that

$$\begin{aligned} \Psi^* \# H \# \Psi(x, p) &= \Psi^*(x) \# \left( H(x, p) \Psi(x) + \frac{iM^{-1/2}}{2} p \cdot \nabla \Psi(x) - \frac{M^{-1}}{4} \Delta \Psi(x) \right) \\ &= \Psi^*(x) H(x, p) \Psi(x) + \frac{iM^{-1/2}}{2} p \cdot \nabla \Psi^*(x) \Psi(x) - \frac{M^{-1}}{4} \Delta \Psi^*(x) \Psi(x) \\ &\quad + \frac{i}{2M^{1/2}} \Psi^*(x) p \cdot \nabla \Psi(x) - \frac{1}{4M} \nabla \Psi^*(x) \cdot \nabla \Psi(x) - \frac{1}{4M} \Psi^*(x) \Delta \Psi(x) \\ &= \Psi^*(x) H(x, p) \Psi(x) + \frac{iM^{-1/2}}{2} p \cdot \nabla (\Psi^*(x) \Psi(x)) \\ &\quad - \frac{M^{-1}}{4} \left( \Delta (\Psi^*(x) \Psi(x)) - \nabla \Psi^*(x) \cdot \nabla \Psi(x) \right) \\ &= \Psi^*(x) H(x, p) \Psi(x) + \frac{M^{-1}}{4} \nabla \Psi^*(x) \cdot \nabla \Psi(x). \end{aligned}$$

□

Define

$$\bar{H}(x, p) := \Psi^* \# H \# \Psi = \Psi^*(x) H(x, p) \Psi(x) + \frac{1}{4M} \nabla \Psi^*(x) \cdot \nabla \Psi(x),$$

which by (3.3) and (3.4) implies  $\hat{\Psi}^* e^{t\alpha \hat{H}} \hat{\Psi} = e^{t\alpha \hat{\bar{H}}}$  and we obtain by (3.1) and (3.2) that

$$\partial_t \hat{A}_t = iM^{1/2} [\hat{\bar{H}}, \hat{A}_t].$$

The next step is to determine  $\Psi$  so that  $\bar{H} = \Psi^* \# H \# \Psi$  is diagonal or approximately diagonal, in order to make  $\bar{H} \bar{A}_t - \bar{A}_t \bar{H}$  small since it appears in the expansion of the compositions in

$$\partial_t \bar{A}_t = iM^{1/2}(\bar{H} \# \bar{A}_t - \bar{A}_t \# \bar{H}).$$

In the case when  $\bar{H}$  diagonal also  $\hat{H}$  is diagonal and then  $\hat{A}$  remains diagonal if it initially is diagonal, since then

$$\frac{d}{dt} \hat{A}_{jk}(t) = iM^{1/2}(\bar{H}_{jj} \hat{A}_{jk}(t) - \hat{A}_{jk}(t) \bar{H}_{kk}) = 0, \text{ for } j \neq k.$$

We have

$$\bar{H}(x, p) = \Psi^*(x) \left( \frac{|p|^2}{2} \mathbf{I} + V(x) + \frac{1}{4M} \Psi(x) \nabla \Psi^*(x) \cdot \nabla \Psi(x) \Psi^*(x) \right) \Psi(x).$$

Therefore the aim is to choose the orthogonal matrix  $\Psi$  so that it is a solution or an approximate solution to the non linear eigenvalue problem

$$(3.6) \quad \left( V + \frac{1}{4M} \Psi \nabla \Psi^* \cdot \nabla \Psi \Psi^* \right) \Psi = \Psi \Lambda$$

where  $\Lambda$  is diagonal with  $\Lambda_{jj} =: \lambda_j$ . Such a transformation  $\Psi$  is an  $\mathcal{O}(M^{-1})$  perturbation of the eigenvectors to  $V(x)$ , provided the eigenvalues  $\tilde{\lambda}_j(x)$  of  $V(x)$  do not cross and  $M$  is sufficiently large. The next section shows that (3.6) has a unique solution, if the potential  $V$  is real analytic, and that the solution can be approximated by an asymptotic expansion.

**3.1. Solution of the nonlinear eigenvalue problem.** This section presents a version of the standard regular perturbation analysis of matrix eigenvalue problems, cf. [7], which shows that the nonlinear eigenvalue problem (3.6) can be written as a nonlinear system of first order partial differential equations solved by Cauchy-Kovalevsky's theorem or by an asymptotic expansion.

Define for small  $\epsilon \in \mathbb{R}$  the matrix  $\check{V}(\epsilon) := \check{V} + \epsilon \check{B}$  where  $\check{V}$  and  $\check{B}$  are real symmetric  $d \times d$  matrices, depending on a parameter  $x \in \mathbb{R}^N$  and on another parameter  $M \in \mathbb{R}$ . Assume also the matrices  $\check{V}$  and  $\check{B}$  are  $m$  times continuously differentiable as a function of  $x$ . Differentiate, with respect to  $\epsilon$ , the eigenvalue problem

$$\check{V}(\epsilon) \psi_k(\epsilon) = \lambda_k(\epsilon) \psi_k(\epsilon),$$

with the eigenvalues  $\lambda_k(\epsilon) \in \mathbb{R}$  and the corresponding normalized real valued eigenvectors  $\psi_k(\epsilon) \in \mathbb{R}^d$ ,  $k = 1, \dots, d$ , to obtain

$$(\check{V}(\epsilon) - \lambda_k(\epsilon)) \psi'_k(\epsilon) = -(\check{V}'(\epsilon) - \lambda'_k(\epsilon)) \psi_k(\epsilon).$$

The scalar product with  $\psi_\ell(\epsilon)$ , where  $\ell \neq k$ , implies the bounded derivatives

$$(3.7) \quad \begin{aligned} \psi_\ell^* \psi'_k(\epsilon) &= \frac{\psi_\ell^*(\epsilon) \check{B} \psi_k(\epsilon)}{\lambda_\ell(\epsilon) - \lambda_k(\epsilon)} \quad \ell \neq k, \\ \lambda'_k(\epsilon) &= \psi_k(\epsilon)^* \check{B} \psi_k(\epsilon). \end{aligned}$$

The remaining component in the  $\psi_k(\epsilon)$  direction becomes zero by the normalization

$$(3.8) \quad 0 = \frac{d}{d\epsilon} (\psi_k(\epsilon)^* \psi_k(\epsilon)) = 2 \operatorname{Re} \left( \left( \frac{d\psi_k(\epsilon)}{d\epsilon} \right)^* \psi_k(\epsilon) \right) = 2 \left( \frac{d\psi_k(\epsilon)}{d\epsilon} \right)^* \psi_k(\epsilon).$$

In particular, the non linear eigenvalue problem (3.6) has

$$\check{B}(x) = \Psi(x) \nabla \Psi^*(x) \cdot \nabla \Psi(x) \Psi^*(x)$$

so that it can be written as the system of  $d^2 + d$  partial differential equations

$$(3.9) \quad \begin{aligned} \frac{\partial}{\partial \epsilon} \Psi_{jk}(x, \epsilon) &= \sum_{\ell \neq k} \Psi_{j\ell}(x, \epsilon) \frac{(\nabla \Psi^*(x, \epsilon) \cdot \nabla \Psi(x, \epsilon))_{\ell k}}{\lambda_\ell(x, \epsilon) - \lambda_k(x, \epsilon)}, \quad 0 < \epsilon < \frac{1}{4M}, \quad j, k = 1, \dots, d, \\ \frac{\partial}{\partial \epsilon} \lambda_k(x, \epsilon) &= (\nabla \Psi^*(x, \epsilon) \cdot \nabla \Psi(x, \epsilon))_{kk}, \quad k = 1, \dots, d, \end{aligned}$$

with the initial data

$$\begin{aligned} \Psi(x, 0) &= \tilde{\Psi}(x), \\ \lambda_k(x, 0) &= \tilde{\lambda}_k(x). \end{aligned}$$

There is a power series solution for large  $M$  in the case that  $V$  is real analytic and the eigenvalues  $\tilde{\lambda}_k$  are distinct for all  $x$ : since then also  $\tilde{\lambda}$  and  $\tilde{\Psi}$  are real analytic and Cauchy-Kovalesky's theorem, see [4], yields a local solution to the nonlinear system of partial differential equations (3.9).

The assumption of distinct eigenvalues  $\lambda_1(0) < \lambda_2(0) < \dots < \lambda_d(0)$  and the combination of (3.8), (3.7), and

$$\psi_k(\epsilon) - \psi_k(0) = \int_0^\epsilon \psi'_k(s) ds$$

establishes, for sufficiently small  $\epsilon$ ,

$$\psi_k(\epsilon) - \psi_k(0) = \mathcal{O}(\epsilon)$$

and differentiation of (3.7), with respect to the parameter  $x \in \mathbb{R}^N$ , yields

$$\sup_{|\gamma| \leq m, x \in \mathbb{R}^N} \|\partial^\gamma (\psi_k(\epsilon) - \psi_k(0))\| = \mathcal{O}(\epsilon).$$

The induction (3.11) uses this estimate for  $\epsilon = 1/(4M)$  in (3.10) and (3.12).

An alternative to solve (3.6) exactly, which requires less regularity on  $V$ , is the following approximate solution based on recursion to obtain an asymptotic expansion. Let  $\mathcal{S}(C)$  denote an orthogonal matrix of eigenvectors to a  $d \times d$  Hermitian matrix  $C$ , with the columns in the order of the eigenvalues, so that e.g.  $\mathcal{S}(V(x)) = [\tilde{\Psi}_1(x) \ \tilde{\Psi}_2(x) \ \dots \ \tilde{\Psi}_d(x)]$  as in (2.4). Let  $\Psi[1] = \mathcal{S}(V(x))$  and define

$$\Psi[j+1] = \mathcal{S}\left((V + \frac{1}{4M} \Psi[j] \nabla \Psi^*[j] \cdot \nabla \Psi[j] \Psi^*[j])(x)\right).$$

Assume that the eigenvalues  $\tilde{\lambda}_j$  of  $V$  are distinct and  $V \in [\mathcal{C}^m(\mathbb{R}^N)]^{d^2}$ . The regular perturbation theory of real symmetric matrices in (3.7) shows that for sufficiently large  $M$  and any  $k \leq m$

$$(3.10) \quad \max_{|\gamma| \leq k-1} \|\partial^\gamma (\Psi[2] - \Psi[1])\|_{L^\infty} = \mathcal{O}_k(M^{-1}),$$

where  $\mathcal{O}_k$  denotes an order relation that is allowed to depend on  $k$ . Then induction in  $j$ , for  $j \leq k$ , shows that

$$(3.11) \quad \max_{|\gamma| \leq k-j} \|\partial^\gamma (\Psi[j+1] - \Psi[j])\|_{L^\infty} \leq C_{k,j} M^{-j}.$$

as follows: we have

$$\begin{aligned} &V + \frac{1}{4M} \Psi[j+1] \nabla \Psi^*[j+1] \cdot \nabla \Psi[j+1] \Psi^*[j+1] \\ &= V + \frac{1}{4M} \Psi[j] \nabla \Psi^*[j] \cdot \nabla \Psi[j] \Psi^*[j] + \mathcal{O}_1(M^{-(j+1)}) \end{aligned}$$

so that regular perturbation theory implies that the left hand side is diagonalized by

$$(3.12) \quad \Psi[j+2] = \Psi[j+1] + \mathcal{O}(M^{-(j+1)})$$

and there is a constant  $K_{k,j}$  such that

$$C_{k,j+1} \leq K_{k,j} C_{k,j}.$$

The choice  $\Psi = \Psi[\kappa]$  implies

$$(3.13) \quad \begin{aligned} \bar{H}(x, p) &= \Psi^*[\kappa] \# H \# \Psi[\kappa] \\ &= \underbrace{\Psi^*[\kappa] \left( \frac{|p|^2}{2} \mathbf{I} + V + \frac{1}{4M} \Psi[\kappa-1] \nabla \Psi^*[\kappa-1] \cdot \nabla \Psi[\kappa-1] \Psi^*[\kappa-1] \right) \Psi[\kappa]}_{=: \frac{|p|^2}{2} \mathbf{I} + \Lambda(x)} \\ &\quad + \frac{1}{4M} \Psi^*[\kappa] \left( \Psi[\kappa] \nabla \Psi^*[\kappa] \cdot \nabla \Psi[\kappa] \Psi^*[\kappa] \right. \\ &\quad \left. - \Psi[\kappa-1] \nabla \Psi^*[\kappa-1] \cdot \nabla \Psi[\kappa-1] \Psi^*[\kappa-1] \right) \Psi[\kappa] \\ &=: \underbrace{\frac{|p|^2}{2} \mathbf{I} + \Lambda(x)}_{=: \bar{H}_0} + \underbrace{r_0}_{\mathcal{O}(M^{-\kappa})}, \end{aligned}$$

where  $\Lambda(x) = \tilde{\Lambda}(x) + \mathcal{O}(M^{-1})$  is diagonal with  $\tilde{\Lambda}_{jj} = \tilde{\lambda}_j$  as in (2.4) and  $r_0$  is the term with the factor  $\frac{1}{4M} \Psi^*[\kappa](\dots) \Psi[\kappa]$ , which only depends on the  $x$ -coordinate. Here  $\kappa \leq m$ , where  $V \in [\mathcal{C}^m(\mathbb{R}^N)]^{d^2}$  and we remind that

$$\bar{H}_0 = \frac{|p|^2}{2} \mathbf{I} + \Lambda(x) = \underbrace{\frac{|p|^2}{2} \mathbf{I} + \tilde{\Lambda}(x)}_{=: \bar{H}} + \mathcal{O}(M^{-1}).$$

We see that

$$\partial_t \hat{A}_t = iM^{1/2} [\hat{H}, \hat{A}_t] = iM^{1/2} [\hat{H}_0, \hat{A}_t] + iM^{1/2} [\hat{r}_0, \hat{A}_t]$$

consists of a diagonal part and a small coupling  $\mathcal{O}(M^{-\kappa+1/2})$  part. This asymptotic recursion for  $\Psi[j]$  is typically not convergent, therefore the error term  $r_0 = \mathcal{O}(M^{-\kappa})$  may be large if  $\kappa$  is large, unless  $M$  is very large, which is a reason to avoid large values of  $\kappa$ .

**3.2. Remainder terms in the Moyal composition.** The following two lemmas estimate remainder terms in the Moyal expansions of the compositions that we will use below.

**Lemma 3.2.** *Assume  $C : \mathbb{R}^{2N} \rightarrow \mathbb{C}^{d \times d}$  and  $D : \mathbb{R}^{2N} \rightarrow \mathbb{C}^{d \times d}$  have up to  $m+1$  derivatives bounded in  $L^2(\mathbb{R}^{2N})$  and in addition  $m+1$  derivatives of one of these functions has bounded Fourier transform in  $L^1(\mathbb{R}^{2N})$ , then the composition has the expansion*

$$C \# D(x, p) = \sum_{n=0}^m \frac{1}{n!} \left( i \frac{\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'}}{2M^{1/2}} \right)^n C(x, p) D(x', p') \Big|_{(x,p)=(x',p')} + r(z),$$

where the remainder  $r \in L^2(\mathbb{R}^{2N})$  satisfies

$$\begin{aligned} & \|r\|_{L^2(\mathbb{R}^{2N})}^2 \\ & \leq \left(\frac{1}{4M}\right)^{m+1} \frac{1}{(m!)^2(2m+1)} \\ & \quad \times \left\| \int_0^1 e^{\frac{is}{M^{1/2}}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} (\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})^{m+1} C(x, p) D(x', p') ds \right\|_{z=z'}^2_{L^2(\mathbb{R}^{2N})} \\ & = \mathcal{O}(M^{-(m+1)}). \end{aligned}$$

If  $C(x, p) = A(x)$  depends only on the  $x$ -coordinate and has  $m+1$  derivatives bounded in  $L^\infty(\mathbb{R}^N)$

(3.14)

$$r(x, p) = \left(\frac{1}{2M^{1/2}}\right)^{m+1} \int_0^1 e^{-\frac{is}{2}M^{-1/2}\nabla_x \cdot \nabla_p} (-i\nabla_x \cdot \nabla_p)^{m+1} A(x) D(x', p) \frac{(1-s)^m}{m!} ds \Big|_{x'=x},$$

and if  $C(x, p) = A(p)$  depends only on the  $p$ -coordinate and has  $m+1$  derivatives bounded in  $L^\infty(\mathbb{R}^N)$

(3.15)

$$r(x, p) = \left(\frac{1}{2M^{1/2}}\right)^{m+1} \int_0^1 e^{\frac{is}{2}M^{-1/2}\nabla_x \cdot \nabla_p} (i\nabla_x \cdot \nabla_p)^{m+1} A(p) D(x, p') \frac{(1-s)^m}{m!} ds \Big|_{p'=p}.$$

**Lemma 3.3.** Assume  $C : \mathbb{R}^{2N} \rightarrow \mathbb{C}^{d \times d}$  and  $D : \mathbb{R}^{2N} \rightarrow \mathbb{C}^{d \times d}$  belong to  $L^2(\mathbb{R}^{2N})$  and in addition one of these functions has its Fourier transform in  $L^1(\mathbb{R}^{2N})$ , then

$$(3.16) \quad \|C \# D\|_{L^2(\mathbb{R}^{2N})} \leq \frac{1}{(2\pi)^{2N}} \min(\|C\|_{L^2(\mathbb{R}^{2N})} \|\mathcal{F}D\|_{L^1(\mathbb{R}^{2N})}, \|\mathcal{F}C\|_{L^1(\mathbb{R}^{2N})} \|D\|_{L^2(\mathbb{R}^{2N})}),$$

and if  $A : \mathbb{R}^N \rightarrow \mathbb{C}^{d \times d}$  depends only on the  $x$ -coordinate (or only on the  $p$ -coordinate) and is bounded in  $L^\infty(\mathbb{R}^N)$

$$(3.17) \quad \begin{aligned} \|A \# D\|_{L^2(\mathbb{R}^{2N})} & \leq \|A\|_{L^\infty(\mathbb{R}^N)} \|D\|_{L^2(\mathbb{R}^N)}, \\ \|D \# A\|_{L^2(\mathbb{R}^{2N})} & \leq \|A\|_{L^\infty(\mathbb{R}^N)} \|D\|_{L^2(\mathbb{R}^N)}. \end{aligned}$$

The proofs of Lemmas 3.2 and 3.3 are in Section 5. The symbol  $\check{A} : [0, \infty) \times \mathbb{R}^{2N} \rightarrow \mathbb{C}^{d^2}$  that satisfies

$$(3.18) \quad \partial_t \check{A}_t = \{\bar{H}_0, \check{A}_t\}, \quad t > 0, \quad \check{A}_0 = \bar{A}_0,$$

approximates  $\bar{A}_t$ , as we shall see in Lemma 3.4 below. By writing the Poisson bracket explicitly, we see that equation (3.18) is a scalar linear hyperbolic partial differential equation for each component:

$$(3.19) \quad \partial_t \check{A}_{jj}(t, x, p) = (\nabla_p \cdot \nabla_{x'} - \nabla_x \cdot \nabla_{p'}) ((\bar{H}_0)_{jj}(x, p) \check{A}_{jj}(t, x', p')) \Big|_{(x', p')=(x, p)}.$$

This partial differential equation can be solved by the method of characteristics, which generates molecular dynamics paths as follows. Let  $\check{A}_{jj}$  be constant along the characteristic

$$(3.20) \quad \check{A}_{jj}(t, z_0) := \check{A}_{jj}(0, z_0^j(z_0))$$

where the characteristic path  $z_t^j = (x_t, p_t)$  solves the Hamiltonian system

$$(3.21) \quad \begin{aligned} \dot{x}_t &= p_t \\ \dot{p}_t &= -\nabla \lambda_j(x_t), \quad t > 0 \end{aligned}$$

with initial data  $(x_0, p_0) = z_0$  and the Hamiltonian  $(\bar{H}_0(x, p))_{jj} = (\frac{|p|^2}{2} \mathbf{I} + \Lambda(x))_{jj} = \frac{|p|^2}{2} + \lambda_j(x)$ . For each  $j$  we have

$$\underbrace{\partial_t \check{A}_{jj}(0, z_t^j(z_0))}_{=\partial_s \check{A}_{jj}(0, z_t^j(z_s))|_{s=0}} = \{(\bar{H}_0)_{jj}(z_0), \check{A}_{jj}(0, z_t^j(z_0))\},$$

where the equality in the left hand side holds because the Hamiltonian system is autonomous and the Poisson bracket in the right hand side is obtained from the chain rule differentiation at  $s = 0$ . We conclude that (3.18) holds for  $\check{A}$  constructed by (3.20).

**Lemma 3.4.** *Assume that the  $d \times d$  matrix symbols  $\bar{A}_0(z)$  and  $\bar{B}_0(z)$  are diagonal and the bounds (3.30), (3.31), (3.32), (3.36), (3.37), (3.46) and (3.47) are satisfied, then there holds*

$$(3.22) \quad \frac{\text{trace}(\hat{A}_\tau \frac{1}{2}(\hat{B}_0 e^{-\hat{H}/T} + e^{-\hat{H}/T} \hat{B}_0) - \widehat{\check{A}(\tau, z) \bar{B}_0 e^{-\bar{H}_0/T}})}{\text{trace}(e^{-\hat{H}/T})} = \mathcal{O}(M^{-\min(1, \kappa-1/2)}).$$

*Proof.* It is useful to split the estimate into two parts

$$(3.23) \quad \begin{aligned} & \text{trace}(\hat{A}_\tau \frac{1}{2}(\hat{B}_0 e^{-\hat{H}/T} + e^{-\hat{H}/T} \hat{B}_0) - \widehat{\check{A}(\tau, z) \bar{B}_0 e^{-\bar{H}_0/T}}) \\ &= \frac{1}{2} \text{trace}(\hat{A}_\tau (\hat{B}_0 e^{-\hat{H}/T} + e^{-\hat{H}/T} \hat{B}_0 - (\widehat{\bar{B}_0 e^{-\bar{H}_0/T}} + e^{-\bar{H}_0/T} \widehat{\bar{B}_0})) \\ & \quad + \text{trace}((\hat{A}_\tau - \widehat{\check{A}(\tau, z)}) \widehat{\bar{B}_0 e^{-\bar{H}_0/T}}) \end{aligned}$$

where the first part is the approximation error of the Gibbs density operator, which is estimated in Step 1, and the second part is the approximation error of the dynamics of the observable, which is estimated in Step 2. Theorems 3.6 and 3.7 use only Step 2, while Theorem 3.5 uses both Step 1 and Step 2.

*Step 1.* Let  $y : [0, \infty) \times \mathbb{R}^{2N} \rightarrow \mathbb{C}^{d^2}$  and  $\bar{y}_i : [0, \infty) \times \mathbb{R}^{2N} \rightarrow \mathbb{C}^{d^2}$ ,  $i = 0, 1, 2$  be defined by

$$\begin{aligned} y(t, z) &= e^{-t\bar{H}_0(z)} \bar{B}_0, \\ \widehat{\bar{y}_0(t, z)} &= e^{-t\hat{H}}, \\ \widehat{\bar{y}_1(t, z)} &= \hat{B}_0 e^{-t\hat{H}}, \\ \widehat{\bar{y}_2(t, z)} &= e^{-t\hat{H}} \hat{B}_0. \end{aligned}$$

Differentiation yields the linear ordinary differential equation, with  $z$  as a parameter,

$$\partial_t y(t, z) = -\bar{H}_0(z) y(t, z), \quad t > 0, \quad y(0, \cdot) = \bar{B}_0.$$

The dynamics of  $\bar{y}_1$  satisfies

$$\partial_t \widehat{\bar{y}_1(t, z)} = \hat{B}_0 \frac{d}{dt} e^{-t\hat{H}} = -\hat{B}_0 e^{-t\hat{H}} \hat{H} = -\widehat{\bar{y}_1(t, z)} \hat{H}$$

and the corresponding evolution equation for  $\bar{y}_1$  is the linear partial differential equation

$$\partial_t \bar{y}_1(t, z) = -\bar{y}_1(t, z) \# \bar{H}(z), \quad t > 0, \quad \bar{y}_1(0, \cdot) = \bar{B}_0,$$

with time-independent generator. Analogously we obtain the equations

$$\begin{aligned} \partial_t \bar{y}_2(t, z) &= -\bar{H}(z) \# \bar{y}_2(t, z), \quad t > 0, \quad \bar{y}_2(0, \cdot) = \bar{B}_0, \\ \partial_t \bar{y}_0(t, z) &= -\bar{H}(z) \# \bar{y}_0(t, z), \quad t > 0, \quad \bar{y}_0(0, \cdot) = \mathbf{I}. \end{aligned}$$

We have the two linear equations

$$\begin{aligned}\partial_t \widehat{\bar{y}_1(t, z)} + \widehat{\bar{y}_1(t, z) \# \bar{H}(z)} &= 0, \quad t > 0, \\ \partial_t \widehat{y(t, z)} + \widehat{y(t, z) \# \bar{H}(z)} &= \widehat{y(t, z) \# \bar{H}(z)} - \widehat{y(t, z) \bar{H}_0(z)}, \quad t > 0,\end{aligned}$$

and Duhamel's principle implies

$$\begin{aligned}(3.24) \quad \hat{y}(t, z) - \widehat{\bar{y}_1(t, z)} &= \int_0^t (y(s, z) \# \bar{H}(z) - y(s, z) \bar{H}_0(z)) \widehat{\bar{y}_0(t-s, z)} ds \\ &= \int_0^t \underbrace{(y(s, z) \# \bar{H}(z) - y(s, z) \bar{H}_0(z))}_{=: \hat{R}_{1s}} e^{-(t-s)\hat{H}} ds.\end{aligned}$$

Similarly we have

$$\begin{aligned}\partial_t \widehat{\bar{y}_2(t, z)} + \widehat{\bar{H}(z) \# \bar{y}_2(t, z)} &= 0, \quad t > 0, \\ \partial_t \widehat{y(t, z)} + \widehat{\bar{H}(z) \# y(t, z)} &= \widehat{\bar{H}(z) \# y(t, z)} - \widehat{y(t, z) \bar{H}_0(z)}, \quad t > 0,\end{aligned}$$

and

$$\begin{aligned}(3.25) \quad \hat{y}(t, z) - \widehat{\bar{y}_2(t, z)} &= \int_0^t \widehat{\bar{y}_0(t-s, z)} (\bar{H}(z) \# y(s, z) - y(s, z) \bar{H}_0(z)) \widehat{\bar{H}(z)} ds \\ &= \int_0^t e^{-(t-s)\hat{H}} \underbrace{(\bar{H}(z) \# y(s, z) - y(s, z) \bar{H}_0(z))}_{=: \hat{R}_{2s}} \widehat{\bar{H}(z)} ds.\end{aligned}$$

The remainder terms satisfy by (3.5)

$$\begin{aligned}(3.26) \quad R_{1s} &= (e^{-s\bar{H}_0} \bar{B}_0) \# \bar{H} - e^{-s\bar{H}_0} \bar{B}_0 \bar{H}_0 \\ &= ((e^{-s\bar{H}_0} \bar{B}_0) \# \bar{H}_0 - e^{-s\bar{H}_0} \bar{B}_0 \bar{H}_0) + (e^{-s\bar{H}_0} \bar{B}_0) \# r_0 \\ &= \left( -\frac{iM^{-1/2}}{2} \{e^{-s\bar{H}_0} \bar{B}_0, \bar{H}_0\} + \underbrace{r_2}_{=O(M^{-1})} \right) + (e^{-s\bar{H}_0} \bar{B}_0) \# r_0 \\ &= \left( -\frac{i}{2M^{1/2}} \bar{B}_0 \underbrace{\{e^{-s\bar{H}_0}, \bar{H}_0\}}_{=0} - \frac{i}{2M^{1/2}} e^{-s\bar{H}_0} \{\bar{B}_0, \bar{H}_0\} + r_2 \right) + (e^{-s\bar{H}_0} \bar{B}_0) \# r_0 \\ &= \left( -\frac{i}{2M^{1/2}} e^{-s\bar{H}_0} \{\bar{B}_0, \bar{H}_0\} + r_2 \right) + (e^{-s\bar{H}_0} \bar{B}_0) \# r_0\end{aligned}$$

and analogously

$$\begin{aligned}(3.27) \quad R_{2s} &= (\bar{H} \# e^{-s\bar{H}_0} \bar{B}_0) - e^{-s\bar{H}_0} \bar{B}_0 \bar{H}_0 \\ &= \left( -\frac{i}{2M^{1/2}} e^{-s\bar{H}_0} \{\bar{H}_0, \bar{B}_0\} + r'_2 \right) + r_0 \# (e^{-s\bar{H}_0} \bar{B}_0),\end{aligned}$$

where  $r'_2 = \mathcal{O}(M^{-1})$ . More precisely (3.14) and (3.15) applied to the  $x$  and  $p$  dependent terms in  $\bar{H}_0$  separately implies

$$\begin{aligned}
(3.28) \quad r_2(x, p, s) &= \frac{-1}{4M} \int_0^1 e^{\frac{i\sigma}{2M^{1/2}}(\nabla_x \cdot \nabla_p)} \left( (\nabla_x \cdot \nabla_p)^2 \left( \frac{|p|^2}{2} \mathbb{I} e^{-s\bar{H}_0(x, p')} \bar{B}_0(x, p') \right) \right. \\
&\quad \left. + (\nabla_x \cdot \nabla_p)^2 (\Lambda(x) e^{-s\bar{H}_0(x', p)} \bar{B}_0(x', p)) \right) \Big|_{\substack{x=x' \\ p=p'}} (1 - \sigma) d\sigma \\
&= \frac{-1}{4M} \int_0^1 e^{\frac{i\sigma}{2M^{1/2}}(\nabla_x \cdot \nabla_p)} \left( e^{-s\bar{H}_0(x, p')} \bar{B}_0(x, p') (s^2 \nabla \Lambda(x) \cdot \nabla \Lambda(x) - s \Delta \Lambda(x)) \right. \\
&\quad - 2s e^{-s\bar{H}_0(x, p')} \nabla \Lambda(x) \cdot \nabla_x \bar{B}_0(x, p') + e^{-s\bar{H}_0(x, p')} \Delta_x \bar{B}_0(x, p') \\
&\quad - s e^{-s\bar{H}_0(x', p)} \bar{B}_0(x', p) \Delta \Lambda(x) \\
&\quad + s^2 e^{-s\bar{H}_0(x', p)} \bar{B}_0(x', p) \sum_{jk} p_j p_k \partial_{x_j} \partial_{x_k} \Lambda(x) \\
&\quad - 2s e^{-s\bar{H}_0(x', p)} \sum_{jk} p_j \partial_{x_j} \partial_{x_k} \Lambda(x) \partial_{p_k} \bar{B}_0(x', p) \\
&\quad \left. + e^{-s\bar{H}_0(x', p)} \sum_{jk} \partial_{x_j} \partial_{x_k} \Lambda(x) \partial_{p_k} \partial_{p_k} \bar{B}_0(x', p) \right)_{x=x', p=p'} (1 - \sigma) d\sigma.
\end{aligned}$$

We have by (3.17) in Lemma 3.3, where  $A$  is the function of  $x$  and  $D$  is the function of  $(x', p')$  in the estimates of  $r_0$  and  $r_2$  in (3.13) and (3.28),

$$\begin{aligned}
\|r_0 \# e^{-s\bar{H}_0} \bar{B}_0\|_{L^2(\mathbb{R}^{2N})} &\leq \|r_0\|_{L^\infty(\mathbb{R}^N)} \|e^{-s\bar{H}_0} \bar{B}_0\|_{L^2(\mathbb{R}^{2N})}, \\
M^{-1/2} \|e^{-s\bar{H}_0} \{\bar{B}_0, \bar{H}_0\}\|_{L^2(\mathbb{R}^{2N})} &= M^{-1/2} \|e^{-s\bar{H}_0} (p \cdot \nabla_x \bar{B}_0 - \nabla \Lambda \cdot \nabla_p \bar{B}_0)\|_{L^2(\mathbb{R}^{2N})}, \\
4M \|r_2\|_{L^2(\mathbb{R}^{2N})} &\leq s \|e^{-s\bar{H}_0} \bar{B}_0(x, p)\|_{L^2(\mathbb{R}^{2N})} \|\Delta \Lambda\|_{L^\infty(\mathbb{R}^{2N})} \\
&\quad + s^2 \sum_{jk} \|p_j p_k e^{-s\bar{H}_0} \bar{B}_0(x, p)\|_{L^2(\mathbb{R}^{2N})} \|\partial_{x_j x_k} \Lambda\|_{L^\infty(\mathbb{R}^{2N})} \\
&\quad + 2s \sum_{jk} \|p_j e^{-s\bar{H}_0} \partial_{p_k} \bar{B}_0(x, p)\|_{L^2(\mathbb{R}^{2N})} \|\partial_{x_j x_k} \Lambda\|_{L^\infty(\mathbb{R}^{2N})} \\
&\quad + \sum_{jk} \|e^{-s\bar{H}_0} \partial_{p_j p_k} \bar{B}_0(x, p)\|_{L^2(\mathbb{R}^{2N})} \|\partial_{x_j x_k} \Lambda\|_{L^\infty(\mathbb{R}^{2N})} \\
&\quad + \|e^{-s\bar{H}_0} \bar{B}_0(x, p) (s^2 \nabla \Lambda \cdot \nabla \Lambda - s \Delta \Lambda)\|_{L^2(\mathbb{R}^{2N})} \\
&\quad + 2s \|e^{-s\bar{H}_0} \nabla \Lambda \cdot \nabla_x \bar{B}_0(x, p)\|_{L^2(\mathbb{R}^{2N})} \\
&\quad + \|e^{-s\bar{H}_0} \Delta_x \bar{B}_0(x, p)\|_{L^2(\mathbb{R}^{2N})}.
\end{aligned}$$

Here we see that  $r_0$  depends only on the  $x$ -coordinate and the composition in  $r_2$  has one factor that also depends only on the  $x$ -coordinate. Therefore, by Lemma 3.2 and (3.17) we obtain

$$(3.29) \quad \|R_{1s}\|_{L^2(\mathbb{R}^{2N})} + \|R_{2s}\|_{L^2(\mathbb{R}^{2N})} = \mathcal{O}(M^{-1/2}),$$

provided there holds

$$(3.30) \quad \|r_0\|_{L^\infty(\mathbb{R}^N)} = \mathcal{O}(M^{-1}),$$



and

$$\begin{aligned}
& \| |\nabla \Lambda|^2 \|_{L^\infty(\mathbb{R}^N)} + \|\Delta \Lambda\|_{L^\infty(\mathbb{R}^N)} + \max_{j,k} \|\partial_{x_j} \partial_{x_k} \Lambda\|_{L^\infty(\mathbb{R}^N)} = \mathcal{O}(1), \\
& \sum_{jk} \sup_{t \in [0, 1/T]} \|e^{-t\bar{H}_0} p_j \partial_{p_k} \bar{B}_0\|_{L^2(\mathbb{R}^{2N})} + \sum_{jk} \sup_{t \in [0, 1/T]} \|e^{-t\bar{H}_0} \partial_{p_j} \partial_{p_k} \bar{B}_0\|_{L^2(\mathbb{R}^{2N})} = \mathcal{O}(1), \\
& \sum_{jk} \sup_{t \in [0, 1/T]} \|e^{-t\bar{H}_0} p_j p_k \bar{B}_0\|_{L^2(\mathbb{R}^{2N})} = \mathcal{O}(1), \\
& \sup_{t \in [0, 1/T]} \|e^{-t\bar{H}_0} \Delta_x \bar{B}_0\|_{L^2(\mathbb{R}^{2N})} + \sup_{t \in [0, 1/T]} \|e^{-t\bar{H}_0} \nabla \Lambda \cdot \nabla_x \bar{B}_0\|_{L^2(\mathbb{R}^{2N})} = \mathcal{O}(1), \\
& \sup_{t \in [0, 1/T]} \|e^{-t\bar{H}_0} \bar{B}_0\|_{L^2(\mathbb{R}^{2N})} = \mathcal{O}(1), \\
& \sup_{t \in [0, 1/T]} \|e^{-t\bar{H}_0} (p \cdot \nabla_x \bar{B}_0 - \nabla \Lambda \cdot \nabla_p \bar{B}_0)\|_{L^2(\mathbb{R}^{2N})} = \mathcal{O}(1).
\end{aligned} \tag{3.31}$$

The Hilbert-Schmidt inner product,  $\text{trace}(\hat{B}^* \hat{C})$ , for symmetric operators on  $L^2(\mathbb{R}^N)$ , and its Cauchy's inequality imply together with (3.24)

$$\begin{aligned}
& \left[ \text{trace} \left( \hat{A}_\tau (\hat{y}(t) - \hat{y}(t)) \right) \right]^2 \\
&= \left( \text{trace} \left( \hat{A}_\tau \int_0^t \hat{R}_{1s} e^{-(t-s)\hat{H}} ds \right) \right)^2 \\
&= \left( \int_0^t \text{trace} (\hat{A}_\tau \hat{R}_{1s} e^{-(t-s)\hat{H}}) ds \right)^2 \\
&\leq \left( \int_0^t \left( \text{trace} (e^{i\tau M^{1/2} \hat{H}} \hat{A}_0^2 e^{-i\tau M^{1/2} \hat{H}}) \text{trace} (e^{-(t-s)\hat{H}} \hat{R}_{1s}^2 e^{-(t-s)\hat{H}}) \right)^{1/2} ds \right)^2 \\
&= \left( \int_0^t \left( \text{trace} (\hat{A}_0^2) \text{trace} (\hat{R}_{1s}^2 e^{-2(t-s)\hat{H}}) \right)^{1/2} ds \right)^2 \\
&\leq \int_0^t \text{trace} (\hat{A}_0^2) ds \int_0^t \text{trace} (\underbrace{(\hat{\Psi} \hat{R}_{1s} \hat{\Psi}^*)^2}_{=: \hat{R}_s} e^{-2(t-s)\hat{H}}) ds.
\end{aligned}$$

Lemma 2.1 establishes

$$\int_0^t \text{trace} (\hat{A}_0^2) ds = t \left( \frac{M^{1/2}}{2\pi} \right)^N \int_{\mathbb{R}^{2N}} \text{trace} (\bar{A}^2(0, z)) dz$$

and we require

$$\|\bar{A}_0\|_{L^2(\mathbb{R}^{2N})} = \mathcal{O}(1). \tag{3.32}$$

The basis  $\{\Phi_n\}_{n=1}^\infty$  of solutions to the Schrödinger equation (2.1) implies

$$\begin{aligned}
\text{trace} (\hat{R}_s^2 e^{-2(t-s)\hat{H}}) &= \sum_{n=1}^\infty \langle \Phi_n, \hat{R}_s^2 e^{-2(t-s)\hat{H}} \Phi_n \rangle \\
&= \sum_{n=1}^\infty \langle \Phi_n, \hat{R}_s^2 \Phi_n \rangle e^{-2(t-s)E_n/T} \\
&\leq e^{-2(t-s)E_1/T} \sum_{n=1}^\infty \langle \Phi_n, \hat{R}_s^2 \Phi_n \rangle \\
&= e^{-2(t-s)E_1/T} \text{trace} (\hat{R}_s^* \hat{R}_s)
\end{aligned}$$

and Lemmas 2.1, 3.2 and (3.17) combined with (3.29) show that

$$(3.33) \quad \begin{aligned} \text{trace}(\hat{R}_s^* \hat{R}_s) &= \left(\frac{M^{1/2}}{2\pi}\right)^N \int_{\mathbb{R}^{2N}} \text{trace}(R_s^* R_s) dz \\ &= \mathcal{O}(M^{-1+N/2}), \end{aligned}$$

so that

$$\text{trace}\left(\hat{A}_\tau(\hat{y}(t) - \hat{y}(t))\right) = \mathcal{O}(M^{-1/2+N/2}).$$

In the special case where  $\bar{A}_0 = \bar{B}_0 = \text{I}$ , we similarly obtain

$$\text{trace}(e^{-\hat{H}/T} - \widehat{e^{-\bar{H}_0/T}}) = \mathcal{O}(M^{-1/2+N/2})$$

and by (2.2)

$$(3.34) \quad \begin{aligned} \text{trace}(\widehat{e^{-\bar{H}_0/T}}) &= \left(\frac{M^{1/2}}{2\pi}\right)^N \int_{\mathbb{R}^{2N}} \text{trace}(e^{-\bar{H}_0(z)/T}) dz, \\ \text{trace}(e^{-\hat{H}/T}) &= \left(\frac{M^{1/2}}{2\pi}\right)^N \left( \int_{\mathbb{R}^{2N}} \text{trace}(e^{-\bar{H}_0(z)/T}) dz + \mathcal{O}(M^{-1/2}) \right). \end{aligned}$$

In conclusion we have for  $M$  sufficiently large

$$\left| \frac{\text{trace}\left(\hat{A}_t((\bar{B}_0 e^{-\bar{H}_0/T})^\wedge - \hat{B}_0 e^{-\hat{H}/T})\right)}{\text{trace}(e^{-\hat{H}/T})} \right| = \mathcal{O}(M^{-1/2}).$$

The more accurate estimate in (3.22) uses, that by (3.24) and (3.25)

$$(3.35) \quad \widehat{y(t, \cdot)} - \frac{1}{2}(\widehat{\bar{y}_1(t, \cdot)} + \widehat{\bar{y}_2(t, \cdot)}) = \frac{1}{2} \int_0^t (\widehat{R_{1s} \bar{y}_0(t-s, \cdot)} + \widehat{\bar{y}_0(t-s, \cdot) R_{2s}}) ds.$$

Let  $r_1 := M^{-1/2} \{\bar{B}_0, \bar{H}_0\} e^{-s\bar{H}_0}$ . The estimate (3.26) shows that the dominating term in  $R_{1s}$  is  $r_1$  and similarly by (3.27) the dominating term in  $R_{2s}$  is  $-r_1$ . By (3.24), applied with  $\bar{B}_0 = \text{I}$ , we obtain

$$\hat{y}_0(s) = \hat{y}(s) + \int_0^s \hat{R}_1(s') \hat{y}_0(s-s') ds',$$

which replaces the remainder term  $\hat{r}_1 \hat{y}_0$  included in (3.24) by the smaller term

$$(r_1 \# y - y \# r_1)^\wedge,$$

present in (3.35) and generates the new remainder terms

$$\begin{aligned} \int_0^t \hat{r}_1 \hat{R}_1 \hat{y}_0 ds &= \int_0^t (r_1 \# R_1)^\wedge \hat{y}_0 ds, \\ \int_0^t \hat{y}_0 \hat{R}_1 \hat{r}_1 ds &= \int_0^t \hat{y}_0 (R_1 \# r_1)^\wedge ds. \end{aligned}$$

Lemma 3.2 and (3.16) imply  $\|r_1 \# y - y \# r_1\|_{L^2(\mathbb{R}^{2N})} = \mathcal{O}(M^{-1})$  provided

$$(3.36) \quad \begin{aligned} \frac{1}{(2\pi)^{2N}} \|\mathcal{F}(\partial_{z_n} e^{-\bar{H}_0})\|_{L^1(\mathbb{R}^{2N})} &= \mathcal{O}(1), \\ \sum_n \|\partial_{z_n}(p \cdot \bar{B}_0 - \nabla \Lambda \cdot \bar{B}_0)\|_{L^2(\mathbb{R}^{2N})} &= \mathcal{O}(1), \end{aligned}$$

and there holds  $\|r_1 \# R_1\|_{L^2(\mathbb{R}^{2N})} + \|R_1 \# r_1\|_{L^2(\mathbb{R}^{2N})} = \mathcal{O}(M^{-1})$  if

$$(3.37) \quad \frac{1}{(2\pi)^{2N}} \|\mathcal{F}(p \cdot \bar{B}_0 - \nabla \Lambda \cdot \bar{B}_0)\|_{L^1(\mathbb{R}^{2N})} = \mathcal{O}(1)$$

and (3.29) are satisfied. We conclude that the first term in the right hand side of (3.23) has the bound  $\mathcal{O}(M^{-1/2})$ , by assuming (3.31), (3.32), (3.46), and (3.47), and the bound  $\mathcal{O}(M^{-1})$  if in addition (3.36) and (3.37) hold.

*Step 2.* This step is analogous to Step 1. We will compare the classical dynamics  $\widehat{y(t, z_0)} := \widehat{\bar{A}(t, z_0)}$  with the quantum dynamics  $\widehat{\bar{A}_t} = e^{itM^{1/2}\hat{H}}\bar{A}_0e^{-itM^{1/2}\hat{H}} =: \widehat{\bar{y}(t, z)}$ . The classical dynamics for the symbol  $y : [0, \infty) \times \mathbb{R}^{2N} \rightarrow \mathbb{C}^{d^2}$  satisfies by (3.18) and (3.20) the linear partial differential equation

$$\partial_t y(t, z) = \{\bar{H}_0(z), y(t, z)\}, \quad t > 0, \quad y(0, \cdot) = \bar{A}_0,$$

that is, we have the diagonal matrix

$$y_{jk}(t, z_0) = \begin{cases} (\bar{A}_0)_{jj}(z_t^j(z_0)) & \text{if } k = j, \\ 0 & \text{if } k \neq j, \end{cases} \quad \text{for } z_0 \in \mathbb{R}^{2N} \text{ and } t \geq 0.$$

The evolution of  $\bar{y} : [0, \infty) \times \mathbb{R}^{2N} \rightarrow \mathbb{C}^{d^2}$  is defined by the quantum dynamics

$$\partial_t \widehat{\bar{y}(t, z)} = iM^{1/2}[\hat{H}, \widehat{\bar{y}(t, z)}], \quad t > 0, \quad \widehat{\bar{y}(0, \cdot)} = \hat{\bar{A}}_0,$$

which implies

$$\partial_t \bar{y}(t, z) = iM^{1/2}(\bar{H}(z) \# \bar{y}(t, z) - \bar{y}(t, z) \# \bar{H}(z)), \quad t > 0, \quad \bar{y}(0, \cdot) = \bar{A}_0.$$

Duhamel's principle yields

$$\begin{aligned} & \widehat{y(t, z)} - \widehat{\bar{y}(t, z)} \\ &= \int_0^t e^{i(t-s)M^{1/2}\hat{H}} \left( \{\bar{H}_0(z), y(s, z)\} - iM^{1/2}(\bar{H} \# y(s, z) - y(s, z) \# \bar{H}) \right) e^{-i(t-s)M^{1/2}\hat{H}} ds \\ &=: \int_0^t e^{i(t-s)M^{1/2}\hat{H}} \hat{R}_s e^{-i(t-s)M^{1/2}\hat{H}} ds. \end{aligned}$$

Since  $y(s, z)$  and  $\bar{H}_0(z)$  are diagonal the expansion of the composition in Lemma 3.2 and (3.17) imply

$$\begin{aligned} (3.38) \quad R_s &= \{\bar{H}_0, y(s, \cdot)\} - iM^{1/2}(\bar{H} \# y(s, \cdot) - y(s, \cdot) \# \bar{H}) \\ &= \underbrace{\{\bar{H}_0, y\} - iM^{1/2}(\bar{H}_0 \# y - y \# \bar{H}_0)}_{=r_2=\mathcal{O}(M^{-1})} - iM^{1/2}(r_0 \# y - y \# r_0) \\ &= r_2 - iM^{1/2}(r_0 \# y - y \# r_0) = \mathcal{O}(M^{-\min(1, \kappa-1/2)}), \end{aligned}$$

where by Lemma 3.2

$$r_2 = \frac{i}{16M} \int_0^1 e^{i\frac{s}{2M^{1/2}}\nabla_x \cdot \nabla_p} \sum_{|\alpha|=3} \partial_x^\alpha \Lambda(x) \partial_p^\alpha y(x', p) \Big|_{x'=x} (1-s)^2 ds,$$

and by (3.17)

$$\begin{aligned} (3.39) \quad \|r_2\|_{L^2(\mathbb{R}^{2N})} &\leq \frac{1}{48M} \sum_{|\alpha|=3} \|\partial_x^\alpha \Lambda\|_{L^\infty(\mathbb{R}^N)} \|\partial_p^\alpha y(t, \cdot)\|_{L^2(\mathbb{R}^{2N})}, \\ \|r_0 \# y - y \# r_0\|_{L^2(\mathbb{R}^{2N})} &\leq 2\|r_0\|_{L^\infty(\mathbb{R}^N)} \|y(t, \cdot)\|_{L^2(\mathbb{R}^{2N})}. \end{aligned}$$

Let  $z(t) = z_t^i$ . To estimate  $\sum_{|\alpha| \leq 3} \|\partial_p^\alpha y(t, \cdot)\|_{L^2(\mathbb{R}^{2N})}$  we use the first order flow  $\nabla_{z_0} z_t^i(z_0) =: z'(t)$ , second order flow  $z''_{i,km}(t) = \partial_{z_k(0)z_m(0)} z(t)$  and third order flow  $z'''(t)$ , which are solutions to the system

$$\begin{aligned} \dot{z}_i(t) &= (J \nabla \bar{H}_0(z_t))_i =: f_i(z_t), \\ z'_{i,k}(t) &= \delta_{ik} + \int_0^t \sum_{k'} f'_{i,k'}(z_s) z'_{k',k}(s) ds, \quad f'_{i,k'}(z) := \partial_{z_{k'}} f_i(z), \\ z''_{i,km}(t) &= \int_0^t \left( \sum_{k'} f'_{i,k'}(z_s) z''_{k',km}(s) + \sum_{k'm'} f''_{i,k'm'}(z_s) z'_{k',k}(s) z'_{m',m}(s) \right) ds, \\ &\quad f''_{i,k'm'}(z) := \partial_{z_{k'} z_{m'}} f_i(z), \\ z'''_{i,kmn}(t) &= \int_0^t \left( \sum_{k'} f'_{i,k'}(z_s) z'''_{k',kmn}(s) + \sum_{k'm'} f''_{i,k'm'}(z_s) z'_{k',k}(s) z''_{m',mn}(s) \right. \\ &\quad + \sum_{k'm'} f''_{i,k'm'}(z_s) z''_{k',kn}(s) z'_{m',m}(s) + \sum_{k'n'} f''_{i,k'n'}(z_s) z'_{k',km}(s) z'_{n',n}(s) \\ &\quad \left. + \sum_{k'm'n'} f'''_{i,k'm'n'}(z_s) z'_{k',k}(s) z'_{m',m}(s) z'_{n',n}(s) \right) ds, \end{aligned}$$

where  $J$  is the  $2N \times 2N$  matrix

$$(3.40) \quad J = \begin{bmatrix} 0 & \mathbf{I} \\ -\mathbf{I} & 0 \end{bmatrix}.$$

By summation and maximization over indices we obtain the integral inequalities

$$\begin{aligned} \max_{ik} |z'_{i,k}(t)| &\leq 1 + \int_0^t \sum_{k'} |f'_{i,k'}(z_s)| \max_{ik} |z'_{i,k}(s)| ds, \\ \max_{ik} \sum_m |z''_{i,km}(t)| &\leq \int_0^t \sum_{k'} |f'_{i,k'}(z_s)| \max_{ik} \sum_m |z''_{i,km}(s)| ds \\ &\quad + \int_0^t \sum_{k'm'} |f''_{i,k'm'}(z_s)| (\max_{ik} |z'_{i,k}(s)|)^2 ds, \\ (3.41) \quad \max_{ik} \sum_{mn} |z'''_{i,kmn}(t)| &\leq \int_0^t \sum_{k'} |f'_{i,k'}(z_s)| \max_{ik} \sum_{mn} |z'''_{i,kmn}(s)| ds \\ &\quad + \int_0^t \sum_{k'm'} |f''_{i,k'm'}(z_s)| \max_{ik} |z'_{i,k}(s)| \max_{ik} \sum_m |z''_{i,km}(s)| ds \\ &\quad + \int_0^t \sum_{k'm'n'} |f'''_{i,k'm'n'}(z_s)| (\max_{ik} |z'_{i,k}(s)|)^3 ds. \end{aligned}$$

The functions  $\max_{ij} \sum_{|\alpha| \leq 2} \partial_{z_0}^\alpha \partial_{z_j} z_i(t, z_0)$  can therefore be estimated as in [5] by Gronwall's inequality, which states: if there is a positive constant  $K$  and continuous positive functions  $\beta, u : [0, \infty) \rightarrow [0, \infty)$  such that  $u(t) \leq K + \int_0^t \beta(s) u(s) ds$  for  $t > 0$ , then  $u(t) \leq K e^{\int_0^t \beta(s) ds}$  for  $t > 0$ . Gronwall's inequality applied to (3.41) implies

$$(3.42) \quad \max_{ij} \sum_{|\alpha| \leq 2} \|\partial_{z_0}^\alpha \partial_{z_j} z_i(t, z_0)\|_{L^\infty(\mathbb{R}^{2N})} = \mathcal{O}(1)$$

provided that

$$(3.43) \quad \max_i \sum_{|\alpha| \leq 3} \|\partial_x^\alpha \partial_{x_i} \lambda_j\|_{L^\infty(\mathbb{R}^N)} = \mathcal{O}(1).$$

The flows  $z', z'', z'''$  determine the derivatives of the diagonal matrix  $y(t, \cdot)$ , using  $a_j(z) := \bar{A}_{jj}(0, z)$ , by

$$(3.44) \quad \begin{aligned} \partial_{z_k} y_{jj}(t) &= \sum_{k'} a'_{j,k'}(z_t) z'_{k',k}(t), \quad a'_{j,k'}(z) := \partial_{z_{k'}} a_j(z), \\ \partial_{z_k z_m} y_{jj}(t) &= \sum_{k'} a'_{j,k'}(z_t) z''_{k',km}(t) + \sum_{k'm'} a''_{j,k'm'}(z_t) z'_{k',k}(t) z'_{m',m}(t), \\ \partial_{z_k z_m z_n} y_{jj}(t) &= \sum_{k'} a'_{j,k'}(z_t) z'''_{k',kmn}(t) + \sum_{k'm'} a''_{j,k'm'}(z_t) z'_{k',k}(t) z''_{m',mn}(t) \\ &\quad + \sum_{k'm'} a''_{j,k'm'}(z_t) z''_{k',kn}(t) z'_{m',m}(t) \\ &\quad + \sum_{k'n'} a''_{j,k'n'}(z_t) z''_{k',km}(t) z'_{n',n}(t) + \sum_{k'm'n'} a'''_{j,k'm'n'}(z_t) z'_{k',k}(t) z'_{m',m}(t) z'_{n',n}(t), \end{aligned}$$

The constant in the right hand side of (3.42) grows typically exponentially with respect to  $t$ , i.e.  $\max_{ij} \sum_{|\alpha| \leq 2} \|\partial_{z_0}^\alpha \partial_{z_j} z_i(t, z_0)\|_{L^\infty(\mathbb{R}^{2N})} \leq e^{ct}$ , where  $c$  is the positive constant in the right hand side of (3.43). The integration with respect to the initial data measure  $dz_0$  can be replaced by integration with respect to  $dz_t$  since the phase-space volume is preserved, i.e. the Jacobian determinant  $|\det(\frac{\partial z_0^j}{\partial z_t^j})| = 1$  is constant for all time, so that

$$\begin{aligned} \int_{\mathbb{R}^{2N}} |\partial_{z_t}^\alpha a_{jj}(0, z_t^j(x_0, p_0))|^2 dz_0 &= \int_{\mathbb{R}^{2N}} |\partial_{z_t}^\alpha \bar{A}_{jj}(0, z_t^j(x_0, p_0))|^2 dz_0 \\ &= \int_{\mathbb{R}^{2N}} |\partial_{z_t}^\alpha \bar{A}_{jj}(0, z_t^j(x_0, p_0))|^2 |\det(\frac{\partial z_0^j}{\partial z_t^j})| dz_t^j \\ &= \int_{\mathbb{R}^{2N}} |\partial_{z_t}^\alpha \bar{A}_{jj}(0, z_t^j)|^2 dz_t^j. \end{aligned}$$

Equation (3.44) and (3.42) therefore imply

$$\begin{aligned}
(3.45) \quad & \sum_{|\alpha|=1} \sqrt{\int_{\mathbb{R}^{2N}} |\partial_{p_0}^\alpha \bar{A}_{jj}(0, z_t^j(x_0, p_0))|^2 dz_0} \\
& \leq \max_{ik} \|\partial_{z_k(0)} z_i(t)\|_{L^\infty(\mathbb{R}^{2N})} \sum_{|\alpha|=1} \|\partial_z^\alpha \bar{A}_{jj}(0, z)\|_{L^2(\mathbb{R}^{2N})}, \\
& \sum_{|\alpha|=2} \sqrt{\int_{\mathbb{R}^{2N}} |\partial_{p_0}^\alpha \bar{A}_{jj}(0, z_t^j(x_0, p_0))|^2 dz_0} \\
& \leq \sum_n \max_{ik} \|\partial_{z_n(0)z_k(0)} z_i(t)\|_{L^\infty(\mathbb{R}^{2N})} \sum_{|\alpha|=1} \|\partial_z^\alpha \bar{A}_{jj}(0, z)\|_{L^2(\mathbb{R}^{2N})} \\
& \quad + \max_{ik} \|\partial_{z_k(0)} z_i(t)\|_{L^\infty(\mathbb{R}^{2N})}^2 \sum_{|\alpha|=2} \|\partial_z^\alpha \bar{A}_{jj}(0, z)\|_{L^2(\mathbb{R}^{2N})}, \\
& \sum_{|\alpha|=3} \sqrt{\int_{\mathbb{R}^{2N}} |\partial_{p_0}^\alpha \bar{A}_{jj}(0, z_t^j(x_0, p_0))|^2 dz_0} \\
& \leq \sum_{mn} \max_{ik} \|\partial_{z_m(0)z_n(0)z_k(0)} z_i(t)\|_{L^\infty(\mathbb{R}^{2N})} \sum_{|\alpha|=1} \|\partial_z^\alpha \bar{A}_{jj}(0, z)\|_{L^2(\mathbb{R}^{2N})} \\
& \quad + \sum_n \max_{ik} \|\partial_{z_n(0)z_k(0)} z_i(t)\|_{L^\infty(\mathbb{R}^{2N})} \max_{ik} \|\partial_{z_k(0)} z_i(t)\|_{L^\infty(\mathbb{R}^{2N})}^2 \sum_{|\alpha|=2} \|\partial_z^\alpha \bar{A}_{jj}(0, z)\|_{L^2(\mathbb{R}^{2N})} \\
& \quad + \max_{ik} \|\partial_{z_k(0)} z_i(t)\|_{L^\infty(\mathbb{R}^{2N})}^3 \sum_{|\alpha|=3} \|\partial_z^\alpha \bar{A}_{jj}(0, z)\|_{L^2(\mathbb{R}^{2N})},
\end{aligned}$$

and (3.42) implies that these right hand sides are bounded provided that

$$\begin{aligned}
(3.46) \quad & \max_i \sum_{|\alpha| \leq 3} \|\partial_x^\alpha \partial_{x_i} \lambda_j\|_{L^\infty(\mathbb{R}^N)} = \mathcal{O}(1), \\
& \sum_{|\alpha| \leq 3} \|\partial_z^\alpha \bar{A}_{jj}(0, \cdot)\|_{L^2(\mathbb{R}^{2N})} = \mathcal{O}(1).
\end{aligned}$$

We note that the assumption on  $\lambda_j$  is compatible with the assumption that  $\tilde{\lambda}_j(x)$  tends to infinity as  $|x| \rightarrow \infty$ , which is imposed to have a discrete spectrum of  $\hat{H}$ . The choice  $\Psi = \Psi[2]$  yields  $\lambda_j = \tilde{\lambda}_j + \mathcal{O}(M^{-1})$ . The eigenvalues  $\lambda_j$  have four bounded derivatives if the eigenvalues  $\tilde{\lambda}_j$  of the potential  $V$  are distinct and also the corresponding eigenvectors  $\Psi[1]$  and  $\Psi[2]$  have four bounded derivatives, which requires the fifth order derivatives of the potential  $V$  to be bounded.

Let  $C(z)$  be the diagonal matrix  $\bar{B}_0(z)e^{-\bar{H}_0(z)/T}$ . Duhamel's representation, Cauchy's inequality for the trace, and Lemma 2.1 establish

$$\begin{aligned}
& \left| \text{trace} \left( \widehat{C}(\widehat{y}(t, z) - \widehat{y}(t)) \right) \right| \\
&= \left| \text{trace} \left( \int_0^t \widehat{C} e^{i(t-s)M^{1/2}\hat{H}} \hat{R}_s e^{-i(t-s)M^{1/2}\hat{H}} ds \right) \right| \\
&= \left| \int_0^t \text{trace}(\widehat{C} e^{i(t-s)M^{1/2}\hat{H}} \hat{R}_s e^{-i(t-s)M^{1/2}\hat{H}}) ds \right| \\
&= \left| \int_0^t \text{trace}(e^{-i(t-s)M^{1/2}\hat{H}} \widehat{C} e^{i(t-s)M^{1/2}\hat{H}} \hat{R}_s) ds \right| \\
&\leq \int_0^t (\text{trace}(e^{-i(t-s)M^{1/2}\hat{H}} \widehat{C}^* \widehat{C} e^{i(t-s)M^{1/2}\hat{H}}) \text{trace}(\hat{R}_s^* \hat{R}_s))^{1/2} ds \\
&= \int_0^t (\text{trace}(\widehat{C}^* \widehat{C}) \text{trace}(\hat{R}_s^* \hat{R}_s))^{1/2} ds \\
&= \left( \frac{M^{1/2}}{2\pi} \right)^N \int_0^t \left( \int_{\mathbb{R}^{2N}} \text{trace}(C^* C) dz \int_{\mathbb{R}^{2N}} \text{trace}(R_s^* R_s) dz \right)^{1/2} ds \\
&= \left( \frac{M^{1/2}}{2\pi} \right)^N \int_0^t \|\bar{B}_0(z)e^{-\bar{H}_0(z)/T}\|_{L^2(\mathbb{R}^{2N})} \|R_s\|_{L^2(\mathbb{R}^{2N})} ds,
\end{aligned}$$

which together with (3.34) prove the second step of the lemma provided also

$$(3.47) \quad \|\bar{B}_0(z)e^{-\bar{H}_0(z)/T}\|_{L^2(\mathbb{R}^{2N})} = \mathcal{O}(1).$$

□

The result in Lemma 3.4 has clear limitations since the error estimate of the approximation of the Gibbs density operator in Step 1 is not uniform in  $N$  and  $T^{-1}$  and the approximation error of the observable dynamics is not uniform in  $\tau$ . This means that many particles and low temperature yields a large approximation error of the density operator. The approximation error of the observable dynamics depends exponentially on time,  $e^{c\tau}$ , but  $c$  is uniform in  $N$  provided the assumptions in Theorem 3.7 holds uniformly in  $N$ .

### 3.3. Three error estimates for canonical quantum correlation observables.

In conclusion by combining (2.6) and Lemma 3.4, using the observables  $\hat{A}_\tau = \hat{\Psi} \hat{A}_\tau \hat{\Psi}^*$  and  $\hat{B} = \hat{\Psi} \hat{B}_0 \hat{\Psi}^*$  and the diagonal Hamiltonian  $\tilde{H} = \bar{H}_0 + \mathcal{O}(M^{-1})$  in (2.5), we have obtained

**Theorem 3.5.** *Assume that  $\bar{A}_0$  and  $\bar{B}_0$  are diagonal, the  $d \times d$  matrix valued Hamiltonian  $H$  has distinct eigenvalues, that  $\Psi = \Psi[2]$  and that the assumptions (3.30), (3.31), (3.32), (3.46), and (3.47) hold, then the canonical ensemble average satisfies*

$$\begin{aligned}
(3.48) \quad & \frac{\frac{1}{2} \text{trace}(\hat{A}_\tau (\hat{B}_0 e^{-\hat{H}/T} + e^{-\hat{H}/T} \hat{B}_0))}{\text{trace}(e^{-\hat{H}/T})} \\
&= \sum_{j=1}^d \int_{\mathbb{R}^{2N}} q_j \bar{A}_{jj}(0, z_\tau^j(z_0)) \bar{B}_{jj}(z_0) \frac{e^{-\tilde{H}_{jj}(z_0)/T}}{\int_{\mathbb{R}^{2N}} e^{-\tilde{H}_{jj}(z)/T} dz} dz_0 + \mathcal{O}(M^{-1/2}),
\end{aligned}$$

where  $z_\tau^j$  solves (3.21) and  $q_j$  is defined in Lemma 2.2. If in addition (3.36) and (3.37) hold then the estimate in (3.48) holds with the more accurate bound  $\mathcal{O}(M^{-1})$  replacing  $\mathcal{O}(M^{-1/2})$ .

We note that if eigenvalue surfaces cross, i.e. if  $\lambda_j(x) = \lambda_{j+1}(x)$  for some  $j$  and  $x$ , then  $\nabla\Psi(x)$  may not be in  $L^2(\mathbb{R}^N)$ . We have assumed that the observable symbols  $\bar{A}_0$  and  $\bar{B}_0$  are diagonal in the same coordinate transformation  $\Psi[\kappa]$  that approximately diagonalizes the Hamiltonian, in the composition way (3.13). Example of observables that cannot be diagonalized by the same transformation as the Hamiltonian are  $A_0(z) = x\Psi_1(x)\Psi_2^*(x)$  and  $B_0(z) = x\Psi_1(x)\Psi_2^*(x)$  and the correlation based on these observables are then not applicable in Theorem 3.5.

It is essential that only the case  $\|A(x)\#C(x,p)\|_{L^2(\mathbb{R}^{2N})}$ , which by (3.17) is bounded by  $\|A\|_{L^\infty(\mathbb{R}^N)}\|C\|_{L^2(\mathbb{R}^{2N})}$ , and not  $\|C(x,p)\#D(x,p)\|_{L^2(\mathbb{R}^{2N})} \leq \frac{1}{(2\pi)^{2N}}\|\mathcal{F}C\|_{L^1(\mathbb{R}^{2N})}\|D\|_{L^2(\mathbb{R}^{2N})}$ , in (3.16), appear in our analysis for the  $\mathcal{O}(M^{-1/2})$  bound in (3.48). An  $L^1$ -bound on the Fourier transform of a function, which is required in (3.36) and (3.37) to obtain the accuracy  $\mathcal{O}(M^{-1})$  in (3.48), is more demanding regarding regularity than the  $L^\infty$ -norm of the function. For instance, we have

$$\begin{aligned} \int_{\mathbb{R}^{2N}} |\mathcal{F}g(\xi)|d\xi &= \int_{\mathbb{R}^{2N}} (1+|\xi|^2)^{(N+1)}|\mathcal{F}g(\xi)|(1+|\xi|^2)^{-(N+1)}d\xi \\ &\leq \|(1+|\xi|^2)^{(N+1)}\mathcal{F}g(\xi)\|_{L^2(\mathbb{R}^{2N})}\|(1+|\xi|^2)^{-(N+1)}\|_{L^2(\mathbb{R}^{2N})} \\ &\leq \mathcal{O}(1)\|(1+\Delta)^{(N+1)}g\|_{L^2(\mathbb{R}^{2N})}. \end{aligned}$$

The eigenvalues  $\Lambda$  and the Laplacian of the eigenvalues are typically proportional to the number of particles, since the Hamiltonian is the energy of the system. Therefore, the corresponding estimates in the first row of (3.31) are bounded by a constant proportional to  $N$ , while (3.46) can be uniform with respect to  $N$ . Also the remainder term  $r_0$ , related to  $4M^{-1}\nabla\Psi^* \cdot \nabla\Psi$  in (3.13), may be proportional to  $N$ .

By comparing instead to the Weyl quantized classical Gibbs density  $\widehat{e^{-\bar{H}_0}/T}$  we have the following more accurate error estimate, that only requires Step 2 in the proof of Lemma 3.4. A motivation for this density operator is on the next section.

**Theorem 3.6.** *Assume that  $\bar{A}_0$  and  $\bar{B}_0$  are diagonal, the  $d \times d$  matrix valued Hamiltonian  $H$  has distinct eigenvalues, that  $\Psi = \Psi[2]$  and that the assumptions (3.30), (3.32), (3.46), and (3.47) hold, then the canonical ensemble average satisfies*

$$\begin{aligned} (3.49) \quad & \frac{\text{trace}(\hat{A}_\tau \hat{\Psi}(\widehat{\bar{B}_0 e^{-\bar{H}_0/T}}) \hat{\Psi}^*)}{\text{trace}(\widehat{\hat{\Psi} e^{-\bar{H}_0/T} \hat{\Psi}^*})} = \frac{\text{trace}(\hat{A}_\tau(\widehat{\bar{B}_0 e^{-\bar{H}_0/T}}))}{\text{trace}(\widehat{e^{-\bar{H}_0/T}})} \\ &= \sum_{j=1}^d \int_{\mathbb{R}^{2N}} q_j \bar{A}_{jj}(0, z_\tau^j(z_0)) \bar{B}_{jj}(z_0) \frac{e^{-(\bar{H}_0)_{jj}(z_0)/T}}{\int_{\mathbb{R}^{2N}} e^{-(\bar{H}_0)_{jj}(z)/T} dz} dz_0 + \mathcal{O}(M^{-1}), \end{aligned}$$

where  $z_\tau^j$  solves (3.21) and  $q_j$  is defined in Lemma 2.2.

By also assuming that the potential  $V$  is real analytic, the nonlinear eigenvalue problem (3.6) can be solved which implies that  $\bar{H} = \bar{H}_0$  is diagonal and the remainder  $r_0 = 0$  vanishes.

**Theorem 3.7.** *Assume that  $V$  is real analytic,  $\bar{A}_0$  and  $\bar{B}_0$  are diagonal, the  $d \times d$  matrix valued Hamiltonian  $H$  has distinct eigenvalues, and that*

$$\begin{aligned} & \max_i \sum_{|\alpha| \leq 3} \|\partial_x^\alpha \partial_{x_i} \lambda_j\|_{L^\infty(\mathbb{R}^N)} = \mathcal{O}(1), \\ & \sum_{|\alpha| \leq 3} \|\partial_z^\alpha \bar{A}_{jj}(0, \cdot)\|_{L^2(\mathbb{R}^{2N})} = \mathcal{O}(1), \\ & \|\bar{B}_0(z) e^{-\bar{H}(z)/T}\|_{L^2(\mathbb{R}^{2N})} = \mathcal{O}(1), \end{aligned}$$



hold, then the canonical ensemble average satisfies

$$\begin{aligned} \frac{\text{trace}(\hat{A}_\tau \hat{\Psi}(\widehat{\bar{B}_0 e^{-\hat{H}/T}}) \hat{\Psi}^*)}{\text{trace}(\hat{\Psi} \widehat{e^{-\hat{H}/T}} \hat{\Psi}^*)} &= \frac{\text{trace}(\hat{A}_\tau(\widehat{\bar{B}_0 e^{-\hat{H}/T}}))}{\text{trace}(\widehat{e^{-\hat{H}/T}})} \\ &= \sum_{j=1}^d \int_{\mathbb{R}^{2N}} q_j \bar{A}_{jj}(0, z_\tau^j(z_0)) \bar{B}_{jj}(z_0) \frac{e^{-\bar{H}_{jj}(z_0)/T}}{\int_{\mathbb{R}^{2N}} e^{-\bar{H}_{jj}(z)/T} dz} dz_0 + \mathcal{O}(M^{-1}), \end{aligned}$$

where  $z_\tau^j$  solves (3.21) and  $q_j$  is defined in Lemma 2.2.

The next section compares the density operator  $e^{-\hat{H}/T}$ , used in Theorem 3.5, to the density operator  $\widehat{e^{-\bar{H}_0/T}}$  in Theorems 3.6 and 3.7.

#### 4. WHICH DENSITY OPERATOR?

If the density operators  $e^{-\hat{H}/T}$  and  $\widehat{e^{-\bar{H}_0/T}}$  would differ only little it would not matter which one we use as a reference. The proof of Theorem 3.5 shows that observables based on these two operators differ  $\mathcal{O}(M^{-1/2})$  when the number of particles,  $N$ , is small compared to  $M$ . Since we do not know if this difference is small for larger number of particles, we may ask which density operator to use. The density operator  $\hat{\rho}_q = e^{-\hat{H}/T}$  is a time-independent solution to the quantum Liouville-von Neumann equation

$$\partial_t \hat{\rho}_t = iM^{1/2}[\hat{\rho}_t, \hat{H}]$$

while the classical Gibbs density  $e^{-\bar{H}_0/T}$  is a time-independent solution to the classical Liouville equation

$$\partial_t \rho_t = -\{\rho_t, \bar{H}_0\}.$$

The corresponding density matrix symbol  $\rho_q$  is not a time-independent solution to the classical Liouville equation, since  $0 = iM^{1/2}(\rho_q \# \bar{H} - \bar{H} \# \rho_q) \neq \{\rho_q, \bar{H}\}$ , and the classical Gibbs density is not a time-independent solution to the quantum Liouville-von Neumann equation, since  $iM^{1/2}(e^{-\bar{H}_0/T} \# \bar{H}_0 - \bar{H}_0 \# e^{-\bar{H}_0/T}) \neq \{e^{-\bar{H}_0/T}, \bar{H}_0\} = 0$ . We are lead to the question which Gibbs density to use and why use any Gibbs measure. This question is analyzed regarding the time-dependence and the classical behavior in the following two subsections.

**4.1. Time-dependence.** One criterion for a density operator is that it is a time independent or approximately time-independent solution to the quantum Liouville-von Neumann equation, so that measurements of the observable at different times do not differ. In order to determine estimates of time derivatives of observables that are uniform in the number of particles,  $N$ , we use an additional assumption, namely that the observable  $C =: \sum_{n=1}^N \tilde{C}_n/N$  is a sum of observables related to each particle,  $n$ , where  $\tilde{C}_n$  depends on  $z_n$  and a set of neighboring coordinates  $N_n$  which is bounded as  $N \rightarrow \infty$ . Let therefore

$$C(z) = \sum_{n=1}^N \frac{\tilde{C}_n(z)}{N}$$

or more generally

$$(4.1) \quad C(z) = \sum_{n=1}^N \tilde{C}_n(z) \omega_n$$

where  $\omega_n \geq 0$  and  $\sum_{n=1}^N \omega_n = 1$  and

$$(4.2) \quad \begin{aligned} \partial_{z_j} \tilde{C}_n(z) &= 0 & \text{for } j \in \{1, 2, 3, \dots, N\} \setminus N_n, \\ |N_n| &= \mathcal{O}(1) & \text{as } N \rightarrow \infty. \end{aligned}$$

The time-independent density operator  $\hat{\rho}_q$  clearly yields  $\partial_t \text{trace}(\hat{\tilde{C}}_n \hat{\rho}_q(t)) = 0$ . Here we verify that the time derivative of a quantum observable based on the density operator  $\widehat{e^{-\tilde{H}_0/T}}$  also is small, namely  $\partial_t \text{trace}(\hat{\tilde{C}}_n \hat{\rho}_t) / \text{trace}(\hat{\rho}_0)|_{t=0} = \mathcal{O}(M^{-1})$ , when the density operator  $\hat{\rho}$  solves the quantum Liouville-von Neumann equation and has the initial value  $\widehat{e^{-\tilde{H}_0/T}}$ . Write  $z = (z', z^\perp) \in \mathbb{R}^{2N}$ , with  $z' \in \mathbb{R}^{2|N_n|}$  and  $z^\perp \in \mathbb{R}^{2(N-|N_n|)}$ . Let  $\widehat{\cdot}'$ ,  $\#'$  and  $\text{trace}'$  denote the Weyl quantization, the Moyal composition operator and the trace with respect to the coordinates  $z' \in \mathbb{R}^{2|N_n|}$ . We have

$$(4.3) \quad \begin{aligned} \frac{\partial_t \text{trace}(\hat{\tilde{C}}_n \hat{\rho}_t)}{\text{trace}(\hat{\rho}_0)} \Big|_{t=0} &= iM^{1/2} \frac{\text{trace}(\widehat{\tilde{C}_n(z')}(e^{-\tilde{H}_0/T} \hat{H} - \hat{H} e^{-\tilde{H}_0/T}))}{\text{trace}(\hat{\rho}_0)} \\ &= iM^{1/2} \frac{\text{trace}((\hat{H} \widehat{\tilde{C}_n(z')}) - \widehat{\tilde{C}_n(z')} \hat{H}) e^{-\tilde{H}_0/T}}{\text{trace}(\hat{\rho}_0)} \\ &= iM^{1/2} \frac{\int_{\mathbb{R}^{2N}} \text{trace}((\bar{H} \#' \tilde{C}_n(z') - \tilde{C}_n(z') \#' \bar{H}) e^{-\tilde{H}_0/T}) dz}{\int_{\mathbb{R}^{2N}} \text{trace}(e^{-\tilde{H}_0/T}) dz} \\ &= iM^{1/2} \frac{\int_{\mathbb{R}^{2(N-|N_n|)}} \text{trace}'((\widehat{\tilde{H}} \widehat{\tilde{C}_n(z')}' - \widehat{\tilde{C}_n(z')}' \widehat{\tilde{H}}) e^{-\tilde{H}_0/T}) dz^\perp}{\int_{\mathbb{R}^{2(N-|N_n|)}} \text{trace}'(e^{-\tilde{H}_0/T}) dz^\perp} \\ &= iM^{1/2} \frac{\int_{\mathbb{R}^{2(N-|N_n|)}} \text{trace}'(\widehat{\tilde{C}_n(z')}' (e^{-\tilde{H}_0/T} \widehat{\tilde{H}}' - \widehat{\tilde{H}}' e^{-\tilde{H}_0/T})') dz^\perp}{\int_{\mathbb{R}^{2(N-|N_n|)}} \text{trace}'(e^{-\tilde{H}_0/T}) dz^\perp} \\ &= iM^{1/2} \frac{\int_{\mathbb{R}^{2N}} \text{trace}(\tilde{C}_n(z') (e^{-\tilde{H}_0/T} \#' \bar{H} - \bar{H} \#' e^{-\tilde{H}_0/T})) dz}{\int_{\mathbb{R}^{2N}} \text{trace}(e^{-\tilde{H}_0/T}) dz} \\ &= iM^{1/2} \frac{\text{trace}(\int_{\mathbb{R}^{2|N_n|}} \tilde{C}_n(z') \int_{\mathbb{R}^{2(N-|N_n|)}} (e^{-\tilde{H}_0/T} \#' \bar{H} - \bar{H} \#' e^{-\tilde{H}_0/T}) dz^\perp dz')}{\int_{\mathbb{R}^{2N}} \text{trace}(e^{-\tilde{H}_0/T}) dz} \\ &= \mathcal{O}(M^{-1}), \end{aligned}$$

where the error term  $\mathcal{O}(M^{-1})$  follows from (3.31), with  $\mathbb{R}^{2N}$  replaced by  $\mathbb{R}^{2|N_n|}$ , based on the bounded number of coordinates  $2|N_n|$  present in  $\tilde{C}_n$  and  $\#'$ . Therefore the error estimate does not depend on derivatives for all  $2N$  coordinates. We conclude that from the perspective of almost time-independent quantum observables, the time-independent  $\hat{\rho}_q$  is optimal and also  $\widehat{e^{-\tilde{H}_0/T}}$  is reasonable when the observables is a sum of observables that depend on  $|N_n| \ll M$  number of coordinates.

**4.2. Why should we use the Gibbs density?** In Statistical Mechanics books the Gibbs density is often derived as the marginal distribution of a subsystem weakly coupled to a heat bath, where the composite system is assumed to have the microcanonical distribution, see [3]. Here we give a variant of this derivation, assuming instead that the marginal distribution of the subsystem is determined by the subsystem Hamiltonian.

In molecular dynamics simulations one often wants to determine properties of a large macroscopic system with many particles, say  $N \sim 10^{23}$ . Such large particle systems cannot yet be simulated in a computer and one may then ask for a setting where a

smaller system has similar properties as the large. Therefore, we seek an equilibrium density matrix that has the property that the marginal distribution for a subsystem has the same density as the whole system. We will below motivate how this assumption leads to the Gibbs measure; in fact it is enough to assume that the marginal distribution for the subsystem has an equilibrium density which is a function of the Hamiltonian for the subsystem.

An equilibrium density operator must commute with the Hamiltonian operator, by the Liouville-von Neumann equation, and consequently it is diagonalized by the same transformation as the Hamiltonian. The diagonalized density operator is then a function of the eigenvalues of the Hamiltonian operator if they are distinct, by mapping the eigenvalues of the Hamiltonian to the eigenvalues of the density operator. Assume that this mapping can be extended to a continuous mapping  $F : \mathbb{R} \rightarrow \mathbb{R}$ . We can then write the density operator as a function of the Hamiltonian, namely  $\hat{\rho} = F(\hat{H})$ , and we assume that  $F$  is continuously differentiable. The classical limit of the density matrix becomes the density  $F(H)$  in phase-space  $\mathbb{R}^{2(N+n)}$ , with coordinates  $z \in \mathbb{R}^{2n}$  and Hamiltonian  $H_s(z)$  in the subsystem and coordinates  $z_b \in \mathbb{R}^{2N}$  and Hamiltonian  $H_b(z_b, z)$  for a large heat bath environment system, i.e.  $N \gg n$ . The whole system has the Hamiltonian  $H(z, z_b) = H_s(z) + H_b(z_b, z)$ . Assume that the Hamiltonian has been diagonalized and consider one component so that the Hamiltonians are scalar valued. The marginal distribution for the subsystem is then

$$\int_{\mathbb{R}^{2N}} \frac{F(H_b(z_b, z) + H_s(z))}{\frac{F(H_b(z_b, z))}{\int_{\mathbb{R}^{2N}} F(H_b(\bar{z}_b, z)) d\bar{z}_b}} \frac{F(H_b(z_b, z))}{\int_{\mathbb{R}^{2N}} F(H_b(\bar{z}_b, z)) d\bar{z}_b} dz_b$$

which by the mean value theorem is equal to

$$\frac{F(H_b(z_b^*, z) + H_s(z))}{\frac{F(H_b(z_b^*, z))}{\int_{\mathbb{R}^{2N}} F(H_b(\bar{z}_b, z)) d\bar{z}_b}}$$

for some  $z_b^* \in \mathbb{R}^{2N}$ . For given  $F$  and  $H_b$  we may write  $H_b(z_b^*, z) = H_b^*(z, H_s(z))$ . The two main assumptions are that the marginal distribution for the subsystem is a function of the subsystem Hamiltonian, i.e. that there is a function  $f$  and a constant  $C$  such that

$$(4.4) \quad f(H_s(z)) = C \frac{F(H_b^*(z, H_s(z)) + H_s(z))}{F(H_b^*(z, H_s(z)))}$$

for all  $z \in \mathbb{R}^{2n}$  and all subsystem Hamiltonians  $H_s$  in some suitable class of functions, and that

$$(4.5) \quad H_b^*(z, H_s(z)) = H_b^*(z, 0) + o(H_s(z))$$

which expresses that the coupling energy between the subsystem and the heat bath is much smaller than the subsystem energy. We obtain with the definitions

$$(4.6) \quad \begin{aligned} L(H) &:= \log F(H), \\ \ell(H) &:= \log f(H), \end{aligned}$$

and  $H_s^* := H_s(z)$  that

$$\ell(H_s^*) = L(H_b^*(z, H_s^*) + H_s^*) - L(H_b^*(z, H_s^*)) + \log C,$$

and note that the assumption that  $F > 0$  is differentiable shows that  $L$  and  $\ell$  also are differentiable. The continuity of  $F$  and  $L$  yields  $\log C = \ell(0)$ , by choosing  $H_s^* = 0$ , so

that

$$\begin{aligned} \frac{\ell(H_s^*) - \ell(0)}{H_s^*} &= \frac{L(H_b^*(z, H_s^*) + H_s^*) - L(H_b^*(z, H_s^*))}{H_s^*} \\ &= \int_0^1 L'(H_b^*(z, H_s^*) + tH_s^*) dt, \end{aligned}$$

which as  $H_s^* \rightarrow 0$  combined with (4.5) and the differentiability of  $\ell$  establishes

$$\ell'(0) = L'(H_b^*(z, 0)), \quad \text{for all } H_b^*(z, 0).$$

Consequently the function  $L'$  is constant. Let the constant be  $-1/T$  so that

$$L(H) = -\frac{H}{T} + \text{constant}, \quad \text{for any } H \in \mathbb{R},$$

and we have by the definition (4.6) obtained the Gibbs density

$$F(H) = \frac{e^{-H/T}}{\int_{\mathbb{R}^{2N}} e^{-H(z)} dz},$$

which by (4.4) shows that also the marginal is the Gibbs distribution

$$f(H) = \frac{e^{-H/T}}{\int_{\mathbb{R}^{2N}} e^{-H(z)} dz}.$$

In conclusion, molecular dynamics simulations often seek the property that the classical equilibrium for the subsystem is the same as for the larger environment, since the subsystem is supposed to model a larger system. We have shown that the classical Gibbs density is the only differentiable function with this property, while we do not know if the symbol for the quantum density matrix  $\rho_q$  has the same property for a large number of particles. Therefore, we prefer to use the Weyl quantized classical Gibbs density  $\widehat{e^{-\hat{H}_0/T}}$  as our reference density, as in Theorems 3.6 and 3.7, since its drawback of a being non time-independent solution to the quantum Liouville-von Neumann equation is mild, in the sense that the time derivative of an observable (4.3) is  $\mathcal{O}(M^{-1})$  small.

## 5. WEYL QUANTIZATION ESTIMATES: PROOF OF LEMMAS 3.2 AND 3.3

The purpose of this section is to prove Lemmas 3.2 and 3.3 that estimate the remainder terms  $r_i$ ,  $i = 0, 2$  in the  $L^2(\mathbb{R}^{2N})$  norm, and avoid derivatives of high order  $N$ , using that the Hilbert-Schmidt norm of operators can be bounded using the  $L^2(\mathbb{R}^{2N})$  norm of their symbols, as illustrated in (2.7) and (2.8). The precise estimates of remainder terms in the Moyal expansion of the composition of two Weyl quantizations are presented here using Hermitian properties of the operator valued exponential  $e^{\frac{i}{2M^{1/2}}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})}$ .

The Moyal expansions, see [13],

$$\begin{aligned} (5.1) \quad A(x) \# D(x, p) &= e^{-\frac{i}{2M^{1/2}} \nabla_{x'} \cdot \nabla_{p'}} A(x + x') D(x, p + p') \Big|_{x'=p'=0}, \\ C(x, p) \# D(x, p) &= e^{\frac{i}{2M^{1/2}} (\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} C(x, p) D(x', p') \Big|_{(x,p)=(x',p')}, \end{aligned}$$

are well defined for the symbols  $A, C$  and  $D$  in the Schwartz class, viewing the exponential as a Fourier multiplier. We begin with the first expansion.

**5.1. The case  $A(x)\#D(x,p)$ .** We study the remainder term for the expansion of the exponential using  $f_{xp}(x',p') := A(x+x')D(x,p+p')$  and apply the Fourier transform  $\mathcal{F}$  defined for  $f(x',p')$  by

$$\mathcal{F}\{f\}(\xi_x, \xi_p) := \int_{\mathbb{R}^{2N}} f(x', p') e^{-i(x' \cdot \xi_x + p' \cdot \xi_p)} dx' dp'.$$

The remainder is based on a Taylor expansion of the exponential function as follows

$$\begin{aligned} (5.2) \quad & e^{-\frac{i}{2M^{1/2}} \nabla_{x'} \cdot \nabla_{p'}} f_{xp}(x', p') \Big|_{x'=p'=0} \\ &= \left(\frac{1}{2\pi}\right)^{2N} \int_{\mathbb{R}^{2N}} \mathcal{F} f_{xp}(\xi_x, \xi_p) e^{\frac{i}{2} M^{-1/2} \xi_x \cdot \xi_p} d\xi_x d\xi_p \\ &= \left(\frac{1}{2\pi}\right)^{2N} \int_{\mathbb{R}^{2N}} \mathcal{F} f_{xp}(\xi_x, \xi_p) \left( \sum_{n=0}^m \left( \frac{i \xi_x \cdot \xi_p}{2M^{1/2}} \right)^n \frac{1}{n!} \right. \\ &\quad \left. + \left( \frac{i \xi_x \cdot \xi_p}{2M^{1/2}} \right)^{m+1} \frac{1}{m!} \int_0^1 (1-s)^m e^{\frac{is}{2} M^{-1/2} \xi_x \cdot \xi_p} ds \right) d\xi_x d\xi_p \\ &= \sum_{n=0}^m \frac{1}{n!} \left( -\frac{i \nabla_{x'} \cdot \nabla_{p'}}{2M^{1/2}} \right)^n f_{xp}(x', p') \Big|_{x'=p'=0} \\ &\quad + \left( \frac{1}{2M^{1/2}} \right)^{m+1} \int_0^1 e^{-\frac{is}{2} M^{-1/2} \nabla_{x'} \cdot \nabla_{p'}} (-i \nabla_{x'} \cdot \nabla_{p'})^{m+1} f_{xp}(x', p') \frac{(1-s)^m}{m!} ds \Big|_{x'=p'=0}. \end{aligned}$$

The remainder is therefore

$$\begin{aligned} (5.3) \quad & r(x, p) \\ &= \left(\frac{1}{2M^{1/2}}\right)^{m+1} \int_0^1 e^{-\frac{is}{2} M^{-1/2} \nabla_{x'} \cdot \nabla_{p'}} (-i \nabla_{x'} \cdot \nabla_{p'})^{m+1} \underbrace{f_{xp}(x', p')}_{A(x+x')B(x,p+p')} \frac{(1-s)^m}{m!} ds \Big|_{x'=p'=0} \\ &= \left(\frac{1}{2M^{1/2}}\right)^{m+1} \int_0^1 e^{-\frac{is}{2} M^{-1/2} \nabla_x \cdot \nabla_p} (-i \nabla_x \cdot \nabla_p)^{m+1} A(x) B(x', p) \frac{(1-s)^m}{m!} ds \Big|_{x'=x}. \end{aligned}$$

**5.2. The case  $C(x,p)\#D(x,p)$ .** As above we obtain

$$\begin{aligned} & C(x,p)\#D(x,p) \\ &= e^{\frac{i}{2M^{1/2}} (\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} C(x,p) D(x', p') \Big|_{(x,p)=(x',p')} \\ &= \sum_{n=0}^m \frac{1}{n!} \left( i \frac{\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'}}{2M^{1/2}} \right)^n C(x,p) D(x', p') \Big|_{(x,p)=(x',p')} \\ &\quad + \left( \frac{i}{2M^{1/2}} \right)^{m+1} \int_0^1 e^{\frac{is}{2} M^{-1/2} (\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} (\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})^{m+1} \\ &\quad \times C(x,p) D(x', p') \Big|_{(x,p)=(x',p')} \frac{(1-s)^m}{m!} ds. \end{aligned}$$

We can therefore write the remainder as

$$\begin{aligned}
R(x, p) &= \left(\frac{i}{2M^{1/2}}\right)^{m+1} \int_0^1 e^{\frac{is}{2}M^{-1/2}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} (\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})^{m+1} \\
&\quad \times C(x, p) D(x', p') \Big|_{(x,p)=(x',p')} \frac{(1-s)^m}{m!} ds \\
&= \int_0^1 e^{\frac{is}{2}M^{-1/2}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} \tilde{R}(x, p, x', p', s) \Big|_{x'=x, p'=p} ds,
\end{aligned}$$

with

$$(5.4) \quad \tilde{R}(x, p, x', p', s) := \left(\frac{i}{2M^{1/2}}\right)^{m+1} (\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})^{m+1} C(x, p) D(x', p') \frac{(1-s)^m}{m!} ds.$$

Cauchy's inequality implies

$$\begin{aligned}
\|R(z)\|_{L^2(\mathbb{R}^{2N})}^2 &= \int_{\mathbb{R}^{2N}} \left| \int_0^1 e^{\frac{is}{2}M^{-1/2}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} \tilde{R}(z, z', s) ds \right|_{z'=z}^2 dz \\
(5.5) \quad &\leq \int_{\mathbb{R}^{2N}} \int_0^1 \left| e^{\frac{is}{2}M^{-1/2}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} \tilde{R}(z, z', s) \right|_{z'=z}^2 ds dz \\
&= \int_0^1 \int_{\mathbb{R}^{2N}} \left| e^{\frac{is}{2}M^{-1/2}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} \tilde{R}(z, z', s) \right|_{z'=z}^2 dz ds.
\end{aligned}$$

**5.3. Estimates of  $\|C \# D\|_{L^2}$  and  $\|A \# D\|_{L^2}$ .** To verify (3.16) we insert in (5.5) the Fourier representation in the sense of distributions of the Dirac delta measure on  $\mathbb{R}^{2N}$ ,  $\delta(z - z') = (2\pi)^{-2N} \int_{\mathbb{R}^{2N}} e^{i\omega \cdot (z - z')} d\omega$ , which implies

$$\begin{aligned}
&e^{\frac{is}{2}M^{-1/2}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} \left( \tilde{R}(z, z', s) e^{i\omega_{x'}(x-x') + i\omega_p(p-p')} \right) \\
(5.6) \quad &= e^{i\omega_{x'}(x-x') + i\omega_p(p-p')} e^{\frac{is}{2}M^{-1/2}((\nabla_{x'} - i\omega_{x'}) \cdot (\nabla_p + i\omega_p) - (\nabla_x + i\omega_x) \cdot (\nabla_{p'} - i\omega_{p'}))} \tilde{R}(z, z', s) \\
&= e^{i\omega_{x'}(x-x') + i\omega_p(p-p')} e^{\frac{is}{2}M^{-1/2}((\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'}) - i\omega_{x'}(\nabla_p + \nabla_{p'}) + i\omega_p(\nabla_x + \nabla_{x'}))} \tilde{R}(z, z', s).
\end{aligned}$$

Integration by parts, property (5.6) and the fact that the differential operators  $\nabla_{x'} \cdot \nabla_p$  and  $\nabla_x \cdot \nabla_{p'}$  commute and are symmetric in  $L^2(\mathbb{R}^{2N})$  show that

$$\begin{aligned}
(5.7) \quad & \int_{\mathbb{R}^{2N}} |e^{\frac{is}{2}M^{-1/2}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} \tilde{R}(z, z', s)|^2_{z=z'} dz \\
&= \int_{\mathbb{R}^{4N}} e^{\frac{-is}{2}M^{-1/2}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} \tilde{R}^*(z, z', s) \\
&\quad \times (e^{\frac{is}{2}M^{-1/2}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} \tilde{R}(z, z', s)) \delta(z - z') dz dz' \\
&= \frac{1}{(2\pi)^{2N}} \int_{\mathbb{R}^{6N}} e^{\frac{-is}{2}M^{-1/2}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} \tilde{R}^*(z, z', s) \\
&\quad \times e^{\frac{is}{2}M^{-1/2}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} \tilde{R}(z, z', s) e^{i\omega_x \cdot (x-x')} e^{i\omega_p \cdot (p-p')} d\omega_x d\omega_p dz dz' \\
&= \frac{1}{(2\pi)^{2N}} \int_{\mathbb{R}^{6N}} \tilde{R}^*(z, z', s) \\
&\quad \times e^{\frac{-is}{2}M^{-1/2}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} (e^{\frac{is}{2}M^{-1/2}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} \tilde{R}(z, z', s) e^{i\omega_x \cdot (x-x')} e^{i\omega_p \cdot (p-p')}) \\
&\quad \times d\omega_x d\omega_p dz dz' \\
&= \frac{1}{(2\pi)^{2N}} \int_{\mathbb{R}^{6N}} \tilde{R}^*(z, z', s) \\
&\quad \times e^{\frac{-is}{2M^{1/2}}((\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'}) - i\omega_x(\nabla_p + \nabla_{p'}) + i\omega_p(\nabla_x + \nabla_{x'}))} \left( e^{\frac{is}{2}M^{-1/2}(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})} \tilde{R}(z, z', s) \right) \\
&\quad \times e^{i\omega_x \cdot (x-x')} e^{i\omega_p \cdot (p-p')} d\omega_x d\omega_p dz dz' \\
&= \frac{1}{(2\pi)^{2N}} \int_{\mathbb{R}^{6N}} \tilde{R}^*(z, z', s) \\
&\quad \times e^{\frac{-is}{2}M^{-1/2}(-i\omega_x(\nabla_p + \nabla_{p'}) + i\omega_p(\nabla_x + \nabla_{x'}))} \tilde{R}(z, z', s) e^{i\omega_x \cdot (x-x')} e^{i\omega_p \cdot (p-p')} d\omega_x d\omega_p dz dz'.
\end{aligned}$$

Let

$$\begin{aligned}
u &= (z + z')/2, \\
v &= (z - z')/2,
\end{aligned}$$

then by (5.4) we can expand its derivative  $(\nabla_{x'} \cdot \nabla_p - \nabla_x \cdot \nabla_{p'})^{m+1}$  and collect the derivatives with respect to  $z$  and  $z'$  in the functions  $\tilde{C}$  and  $\tilde{D}$  as

$$\tilde{R}(z, z', s) = \sum_{n=1}^{m+1} \tilde{C}_n(z) \tilde{D}_n(z') = \sum_{n=1}^{m+1} \tilde{C}_n(u+v) \tilde{D}_n(u-v) =: r(u, v).$$

The Fourier transform in the  $u$ -direction is the convolution

$$\begin{aligned}
\hat{r}(\xi, v) &:= \sum_{n=1}^{m+1} \int_{\mathbb{R}^{2N}} \tilde{C}_n(u+v) \tilde{D}_n(u-v) e^{-i\xi \cdot u} du \\
&= \frac{1}{(2\pi)^{2N}} \sum_{n=1}^{m+1} \int_{\mathbb{R}^{2N}} e^{i\xi \cdot v} \mathcal{F} \tilde{C}_n(\zeta) e^{-i(\xi - \zeta) \cdot v} \mathcal{F} \tilde{D}_n(\xi - \zeta) d\zeta.
\end{aligned}$$

The right hand side in (5.7) becomes

$$\begin{aligned}
(5.8) \quad & \frac{1}{(2\pi)^{2N}} \int_{\mathbb{R}^{6N}} \tilde{R}^*(z, z', s) \\
& \times e^{\frac{-is}{2}M^{-1/2}(-i\omega_x(\nabla_p + \nabla_{p'}) + i\omega_p(\nabla_x + \nabla_{x'}))} \tilde{R}(z, z', s) e^{i\omega_{x'}(x-x')} e^{i\omega_p(p-p')} d\omega_x d\omega_p dz dz' \\
& = \frac{1}{\pi^{2N}} \int_{\mathbb{R}^{6N}} r^*(u, v) e^{\frac{-is}{4}M^{-1/2}(-iJ\omega \cdot \nabla_u) + 2i\omega \cdot v} r(u, v) d\omega du dv \\
& = \frac{1}{\pi^{2N}(2\pi)^{2N}} \int_{\mathbb{R}^{6N}} \hat{r}^*(\xi, v) e^{\frac{-is}{4}M^{-1/2}(J\omega \cdot \xi) + 2i\omega \cdot v} \hat{r}(\xi, v) d\omega d\xi dv \\
& = \frac{1}{\pi^{2N}} \int_{\mathbb{R}^{4N}} \hat{r}^*(\xi, v) \hat{r}(\xi, v) \delta(2v - \frac{s}{4}M^{-1/2}J\xi) d\xi dv \\
& = \frac{1}{(2\pi)^{2N}} \int_{\mathbb{R}^{2N}} |\hat{r}(\xi, \frac{s}{8}M^{-1/2}J\xi)|^2 d\xi,
\end{aligned}$$

using definition (3.40) of the matrix  $J$ .

The next step is to determine  $\hat{r}(\xi, \gamma J\xi) =: \sum_{n=1}^{m+1} \hat{r}_n(\xi, \gamma J\xi)$  for  $\gamma := \frac{s}{8}M^{-1/2}$  by using the convolution

$$\begin{aligned}
|\hat{r}_n(\xi, v)| &= \frac{1}{(2\pi)^{2N}} \left| \int_{\mathbb{R}^{2N}} \mathcal{F}C_n(\zeta) e^{i\zeta \cdot v} \mathcal{F}D_n(\xi - \zeta) e^{-i(\xi - \zeta) \cdot v} d\zeta \right| \\
&\leq \frac{1}{(2\pi)^{2N}} \int_{\mathbb{R}^{2N}} |\mathcal{F}C_n(\zeta)| |\mathcal{F}D_n(\xi - \zeta)| d\zeta
\end{aligned}$$

which by Young's inequality, namely  $\|f * g\|_{L^2} \leq \|f\|_{L^2} \|g\|_{L^1}$ , implies

$$\begin{aligned}
& \frac{1}{(2\pi)^{2N}} \int_{\mathbb{R}^{2N}} |\hat{r}_n(\xi, \frac{s}{8}M^{-1/2}J\xi)|^2 d\xi \\
&= \frac{1}{(2\pi)^{6N}} \min(\|\mathcal{F}\tilde{C}_n\|_{L^2(\mathbb{R}^{2N})}^2 \|\mathcal{F}\tilde{D}_n\|_{L^1(\mathbb{R}^{2N})}^2, \|\mathcal{F}\tilde{C}_n\|_{L^1(\mathbb{R}^{2N})}^2 \|\mathcal{F}\tilde{D}_n\|_{L^2(\mathbb{R}^{2N})}^2) \\
&= \frac{1}{(2\pi)^{4N}} \min(\|\tilde{C}_n\|_{L^2(\mathbb{R}^{2N})}^2 \|\tilde{D}_n\|_{L^1(\mathbb{R}^{2N})}^2, \|\tilde{C}_n\|_{L^1(\mathbb{R}^{2N})}^2 \|\tilde{D}_n\|_{L^2(\mathbb{R}^{2N})}^2)
\end{aligned}$$

that proves (3.16) in Lemma 3.3 and combined with (5.5), (5.7) and (5.8) it also establishes Lemma 3.2.



The estimate (3.17) of  $\|A(x)\#D(x, p)\|_{L^2(\mathbb{R}^{2N})}$  follows similarly from (5.3) by the Fouriertransform,  $\mathcal{F}_p$ , in the  $p$ -direction

$$\begin{aligned}
& \int_{\mathbb{R}^{2N}} \left| e^{\frac{i}{M^{1/2}} \nabla_x \cdot \nabla_p} A(x) D(x', p) \right|_{x'=x}^2 dx dp \\
&= \int_{\mathbb{R}^{3N}} e^{\frac{-i}{M^{1/2}} \nabla_x \cdot \nabla_p} A^*(x) D^*(x', p) \left( e^{\frac{i}{M^{1/2}} \nabla_x \cdot \nabla_p} A(x) D(x', p) \right) \delta(x - x') dx dx' dp \\
&= \frac{1}{(2\pi)^N} \int_{\mathbb{R}^{4N}} A^*(x) D^*(x', p) e^{\frac{-i}{M^{1/2}} \nabla_x \cdot \nabla_p} \left( e^{\frac{i}{M^{1/2}} \nabla_x \cdot \nabla_p} A(x) D(x', p) e^{i\omega(x-x')} \right) dx dx' dp d\omega \\
&= \frac{1}{(2\pi)^N} \int_{\mathbb{R}^{4N}} A^*(x) D^*(x', p) e^{\frac{-i}{M^{1/2}} (\nabla_x + i\omega) \cdot \nabla_p} \left( e^{\frac{i}{M^{1/2}} \nabla_x \cdot \nabla_p} A(x) D(x', p) \right) e^{i\omega(x-x')} dx dx' dp d\omega \\
&= \frac{1}{(2\pi)^{2N}} \int_{\mathbb{R}^{4N}} A^*(x) \mathcal{F}_p D^*(x', \xi) e^{\frac{i}{M^{1/2}} \omega \cdot \xi} A(x) \mathcal{F}_p D(x', \xi) e^{i\omega(x-x')} dx dx' d\xi d\omega \\
&= \frac{1}{(2\pi)^N} \int_{\mathbb{R}^{3N}} A^*(x) \mathcal{F}_p D^*(x', \xi) A(x) \mathcal{F}_p D(x', \xi) \delta(x - x' + M^{-1/2} \xi) dx dx' d\xi \\
&= \frac{1}{(2\pi)^N} \int_{\mathbb{R}^{2N}} A^*(x' - M^{-1/2} \xi) \mathcal{F}_p D^*(x', \xi) A(x' - M^{-1/2} \xi) \mathcal{F}_p D(x', \xi) dx' d\xi \\
&\leq \frac{1}{(2\pi)^N} \int_{\mathbb{R}^{2N}} |A(x' - M^{-1/2} \xi)|^2 |\mathcal{F}_p D^*(x', \xi)|^2 dx' d\xi \\
&\leq \|A\|_{L^\infty(\mathbb{R}^N)}^2 \|D\|_{L^2(\mathbb{R}^{2N})}^2.
\end{aligned}$$

The case  $A(p)\#D(x, p)$  is analogous to  $A(x)\#D(x, p)$ .

In conclusion, these estimates bound the remainder symbols  $r_0$  and  $r_2$  used in Lemma 3.4. Finally, using that Schwartz functions are dense in  $L^p(\mathbb{R}^{2N})$ , for any  $p \geq 1$ , we have proved Lemmas 3.2 and 3.3.

## 6. NUMERICAL TESTS

In this section we present some numerical tests of the results in this paper. First we formulate a simple model to compare the Schrödinger density with the molecular dynamics density. Then we present a similar model for comparing the Schrödinger position observable correlation with the molecular dynamics position observable correlation. Finally we describe the respective numerical methods, the numerical results and conclusions.

**6.1. A model for equilibrium position observables.** In this section focus is on equilibrium position observables and not on correlations.

Consider a Hamiltonian  $\hat{H} = -M^{-1}I\Delta + V(x)$ , where  $V : \mathbb{R} \rightarrow \mathbb{R}^{2 \times 2}$  and  $I$  is the  $2 \times 2$  identity matrix. Then form the Schrödinger eigenvalue equation  $\hat{H}\Phi_n = E_n\Phi_n$ , where  $E_n \in \mathbb{R}$  and  $\Phi_n : \mathbb{R} \rightarrow \mathbb{R}^2$ . The goal is to numerically test estimate (3.48) for observables  $g : \mathbb{R} \rightarrow \mathbb{R}$  depending only on position. We show in a numerical simulation that also the corresponding densities

$$\frac{\int_{\mathbb{R}} \sum_n g(x) |\Phi_n(x)|^2 e^{-E_n/T} dx}{\int_{\mathbb{R}} \sum_n |\Phi_n(\bar{x})|^2 e^{-E_n/T} d\bar{x}}$$

and

$$\sum_{k=1}^2 q_k \int_{\mathbb{R}} g(x) \frac{e^{-\lambda_k(x)} dx}{\int_{\mathbb{R}} e^{-\lambda_j(\bar{x})/T} d\bar{x}}$$

are very close for large mass  $M$ . Here  $\lambda_k(x)$  is the  $k$ 'th eigenvalue of  $V(x)$ , such that  $\lambda_1(x) \leq \lambda_2(x)$ , and

$$q_k = \frac{\int_{\mathbb{R}} e^{-\lambda_k(x)/T} dx}{\sum_{j=1}^2 \int_{\mathbb{R}} e^{-\lambda_j(x)/T} dx}.$$

We choose to construct an example potential  $V$  that yields an avoided crossing with a variable spectral gap depending on a parameter  $\delta \in \mathbb{R}$ . The construction is done in such a way that the smallest energy gap,  $2\delta$ , appears in only one position,  $x = 0$ . Consider the matrix

$$(6.1) \quad \bar{V}(x) = \begin{bmatrix} x + x^2 & \delta \\ \delta & -x + x^2 \end{bmatrix}, \quad x \in \mathbb{R},$$

with the eigenvalues

$$\bar{\lambda}_1(x) = x^2 - \sqrt{\delta^2 + x^2}, \quad \bar{\lambda}_2(x) = x^2 + \sqrt{\delta^2 + x^2}$$

and the normalized eigenvectors  $\psi_1 := \bar{\psi}_1 / \|\bar{\psi}_1\|_2$ ,  $\psi_2 := \bar{\psi}_2 / \|\bar{\psi}_2\|_2$  where

$$(6.2) \quad \bar{\psi}_1 = \begin{bmatrix} \frac{x - \sqrt{\delta^2 + x^2}}{\delta} \\ 1 \end{bmatrix}, \quad \bar{\psi}_2 = \begin{bmatrix} \frac{x + \sqrt{\delta^2 + x^2}}{\delta} \\ 1 \end{bmatrix}.$$

The derivatives with respect to  $x$  of the eigenvectors  $\psi_1$  and  $\psi_2$  are of order  $1/\delta$ . We want to study the effect of the size of the spatial derivative of the eigenvalues. Therefore we construct a family of matrices with the eigenvalues

$$(6.3) \quad \lambda_1(x) := \bar{\lambda}_1(x) + a \cos(bx) - 1, \quad \lambda_2(x) := \bar{\lambda}_2(x),$$

illustrated in Figure 1(a). Define  $D := \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}$  and  $\Psi := [\psi_1 \quad \psi_2]$ . Then the potential matrix

$$V := \Psi D \Psi^*$$

has the eigenvalues (6.3) and the eigenvectors (6.2).

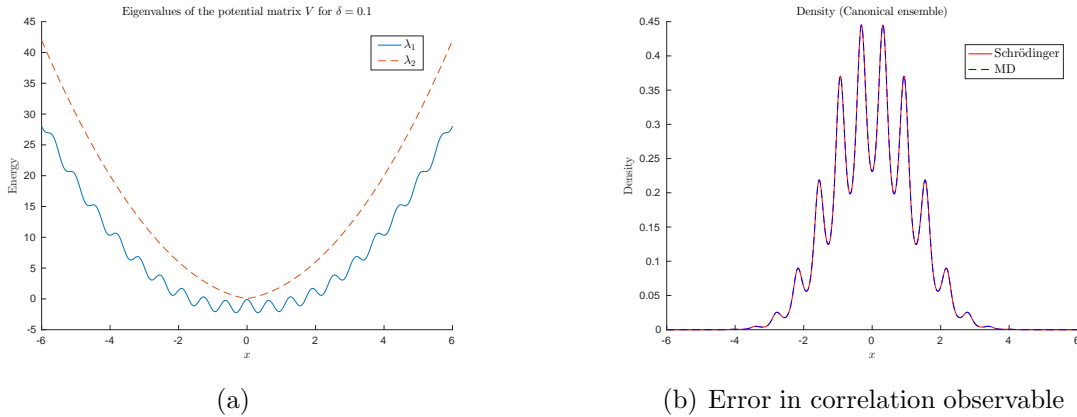


FIGURE 1. (a) The eigenvalue functions  $\lambda_1$  and  $\lambda_2$  of  $V$  for  $\delta = 0.1$ . (b) The densities in (6.7) and (6.8) plotted for  $T = 1.9946$ ,  $\delta = 0.1$  and  $M = 1000$  nearly coincide.

**6.2. A model for time correlated observables.** The aim is to numerically test the correlation of the position observable  $x_0$  at time 0 with the position observable  $x_\tau$  at time  $\tau$ . The time evolution of the position observable operator is defined as

$$\hat{x}_\tau := e^{i\tau\sqrt{M}\hat{H}}\hat{x}_0e^{-i\tau\sqrt{M}\hat{H}}.$$

The error estimate to be tested is (3.49), which in this model is given by

$$(6.4) \quad \frac{\frac{1}{2}\text{trace}\left(\hat{x}_\tau\left(\hat{x}_0e^{-\hat{H}/T} + e^{-\hat{H}/T}\hat{x}_0\right)\right)}{\text{trace}\left(e^{-\hat{H}/T}\right)} = \sum_{j=1}^2 \int_{\mathbb{R}^2} q_j x_\tau^j(z_0) x_0^j(z_0) \frac{e^{-(\frac{|p_0|^2}{2} + \lambda_j(x_0))/T}}{\int_{\mathbb{R}^2} e^{-(\frac{|p|^2}{2} + \lambda_j(x))/T} dz} dz_0 + \mathcal{O}(M^{-1}),$$

where  $z_\tau^j = (x_\tau^j, p_\tau^j)$  solves the Hamiltonian dynamics

$$(6.5) \quad \begin{cases} \dot{x}_\tau^j = p_\tau^j \\ \dot{p}_\tau^j = -\frac{d}{dx_\tau^j} \lambda_j(x_\tau^j), \quad \tau > 0 \end{cases}$$

with the initial condition  $z_0^j = (x_0, p_0) = z_0$ , and  $\lambda_j$  is as in Section 6.1.

**6.3. A numerical simulation for the equilibrium position observables.** Let  $x_k = -6 + k\Delta x$ ,  $k = 0, 1, 2, \dots, N$ , be a discretization of  $[-6, 6]$  where  $\Delta x = \frac{12}{N}$ . We use  $N = 751$ . Make the approximations  $\Phi_n(x_k) \simeq (\phi_{n,k,1} \ \phi_{n,k,2})^*$ ,  $\phi_{n,0,i} = \phi_{n,N,i} = 0$  for  $i = 1, 2$ , and  $E_n \simeq e_n$ . Then

$$\text{I}\Delta\Phi_n(x_k) \simeq \begin{bmatrix} \frac{\phi_{n,k+1,1} - 2\phi_{n,k,1} + \phi_{n,k-1,1}}{(\Delta x)^2} & 0 \\ 0 & \frac{\phi_{n,k+1,2} - 2\phi_{n,k,2} + \phi_{n,k-1,2}}{(\Delta x)^2} \end{bmatrix}.$$

Define  $h_{ij,k} := 2M(\Delta x)^2 V_{ij}(x_k)$ , the matrix

$$H_d := \frac{1}{2M(\Delta x)^2} \begin{bmatrix} h_{11,0+2} & h_{12,0} & -1 & & & & \\ h_{21,0} & h_{22,0+2} & 0 & -1 & & & \\ -1 & 0 & h_{11,1+2} & h_{12,1} & -1 & & \\ & -1 & h_{21,1} & h_{22,1+2} & 0 & -1 & \\ & 0 & & & -1 & 0 & h_{11,N+2} & h_{12,N} \\ & & & & & -1 & h_{21,N} & h_{22,N+2} \end{bmatrix},$$

and the vector

$$\phi_n := \begin{pmatrix} \phi_{n,0,1} \\ \phi_{n,0,2} \\ \phi_{n,1,1} \\ \phi_{n,1,2} \\ \vdots \\ \vdots \\ \phi_{n,N,1} \\ \phi_{n,N,2} \end{pmatrix}.$$

The difference approximation of the Schrödinger equation  $\hat{H}\Phi_n = E_n\Phi_n$  in matrix form becomes

$$(6.6) \quad H_d \phi_n = e_n \phi_n$$

which we solve by using the **Matlab** function **eig** for  $a = 1$  and  $b = 10$  in the eigenvalues (6.3).

Approximate the quantum density in space,  $\frac{\sum_n |\Phi_n(x)|^2 e^{-E_n/T}}{\int_{\mathbb{R}} \sum_n |\Phi_n(x)|^2 e^{-E_n/T} dx}$ , at  $x = -6 + k\Delta x$  with

$$(6.7) \quad \frac{\sum_n (|\phi_{n,k,1}|^2 + |\phi_{n,k,2}|^2) e^{-e_n/T}}{\sum_k \sum_n (|\phi_{n,k,1}|^2 + |\phi_{n,k,2}|^2) e^{-e_n/T} \Delta x}, \quad k = 0, 1, \dots, N.$$

We choose  $x_0, x_N$  far enough away from 0 so that the imposed Dirichlet boundary conditions only affect the solution slightly. To approximate the integrals

$$(6.8) \quad \sum_{k=1}^2 q_k \frac{e^{-\frac{\lambda_k(x)}{T}}}{\int_{\mathbb{R}} e^{-\frac{\lambda_k(x)}{T}} dx},$$

$$q_k = \frac{\int_{\mathbb{R}} e^{-\frac{\lambda_k(x)}{T}} dx}{\sum_{j=1}^2 \int_{\mathbb{R}} e^{-\frac{\lambda_j(x)}{T}} dx}.$$

we use the trapezoidal rule.

**6.4. A numerical simulation for the time correlated observables.** We use the constants  $T = 1.9947$  and  $\delta = 0.1$  which together imply  $q_1 = 0.8$  and treat the left and the right hand sides of the estimate (6.4) separately. In the estimate (6.4) there is the expression  $\text{trace}(\hat{x}_\tau \hat{x}_0 e^{-\hat{H}/T})$  where  $\hat{x}_\tau = e^{i\tau\sqrt{M}\hat{H}} \hat{x}_0 e^{-i\tau\sqrt{M}\hat{H}}$  for which we introduce the approximations

$$e^{i\tau\sqrt{M}\hat{H}} \simeq e^{i\tau\sqrt{M}H_d},$$

$$e^{-\hat{H}/T} \simeq e^{-\frac{H_d}{T}},$$

and

$$\hat{x}_0 \simeq \begin{bmatrix} x_0 & & & & 0 \\ & x_0 & & & \\ & & x_1 & & \\ & & & x_1 & \\ & & & & \ddots \\ 0 & & & & & x_N \\ & & & & & & x_N \end{bmatrix} =: X.$$

Define the matrices

$$P := [\phi_1 \quad \phi_2 \quad \phi_3 \quad \cdots \quad \phi_{2N}], \quad D := \begin{bmatrix} e_1 & & & 0 \\ & e_2 & & \\ & & \ddots & \\ 0 & & & e_{2N} \end{bmatrix}$$

where  $\phi_1, \dots, \phi_N$  and  $e_1, \dots, e_N$  solve equation (6.6) with the partition  $x_k = k\Delta x$ ,  $k = 0, 1, 2, \dots, 2048 = N$  of  $[-4.5, 4.5]$  for  $\Delta x = \frac{9}{N}$ . Note that the orthogonal matrix  $P$  diagonalizes the real symmetric matrix  $H_d$ , so  $H_d = PDP^*$ . Thus

$$e^{i\tau\sqrt{M}H_d} = P e^{i\tau\sqrt{M}D} P^*$$

and

$$e^{-\frac{H_d}{T}} = P e^{-D/T} P^*.$$

We approximate the left hand side of (6.4) by

$$\frac{\text{trace} \left( P e^{i\tau\sqrt{M}D} P^* X P e^{i\tau\sqrt{M}D} P^* (X P e^{-D/T} P^* + P e^{-D/T} P^* X) \right)}{\text{trace} (2P e^{-D/T} P^*)}$$

and perform the calculations in **Matlab**.

For the right hand side of estimate (6.4) we do the computations on a parallel computer using MPI in C programming language and solve the Hamilton dynamics (6.5) using a position Verlet scheme.

Let  $(x_k, p_l) = (k\Delta x, l\Delta p)$  be a partition of  $[-4.5, 4.5] \times [-4.5, 4.5]$  where

$$\Delta x = \frac{9}{N_x - 1}, \Delta p = \frac{9}{N_p - 1} \text{ and } N_x = N_p = 1000.$$

Compute for each  $k, l \in \{-500, -499, \dots, 499, 500\}$  the path from the dynamic (6.5). We do the computations in parallel by a linear distribution of the  $k$ -values to the processes.

We compute the integrals on the right hand side of estimate (6.4) with the 2-dimensional trapezoidal method.

**6.5. Numerical results and conclusions.** We present plots of the densities (6.7) and (6.8), for  $T = 1.9946, \delta = 0.1$  and  $M = 1000$ , in Figure 1(b). The figure shows that the densities, up to the picture resolution, coincide. The domain of the densities is large enough so that the densities are approximately 0 at the endpoints of the domain.

In Figure 2 we show the  $L^1$ -error and the  $L^\infty$ -error of the molecular dynamics density compared to the Schrödinger density with respect to the mass ratio  $M$ . Both errors are inverse proportional to the mass ratio  $M$ . The temperature  $T$  and the gap  $\delta$  are chosen so that  $q_1 = 0.8$ . In neither of the norms, in Figure 2, can we see a  $\delta$  dependency in the error while in theory the constant in  $\mathcal{O}(M^{-1})$  depends on the derivatives, and higher derivatives, of the eigenvectors and eigenvalues of  $V$ . In this case the eigenvector derivative of order  $n$  is  $\mathcal{O}(\delta^{-n})$ .

With the same values for  $T$  and  $\delta$  we show the position observable correlations for different correlation times  $\tau$ , and three different mass ratios  $M$ , in Figure 3(a). For larger mass ratios  $M$  the molecular dynamics position observable correlation gives a better approximation of the Schrödinger position observable correlation.

The  $L^\infty$ -error of the molecular dynamics position observable correlation compared to the Schrödinger position observable correlation, with respect to the mass ratio  $M$  for correlation time  $\tau = 0.2$  is illustrated in Figure 3(b). The largest mass ratio we compute is  $M = 100$ . Note in Figure 3(b) that the  $L^\infty$ -error is inverse proportional to the mass ratio  $M$ .

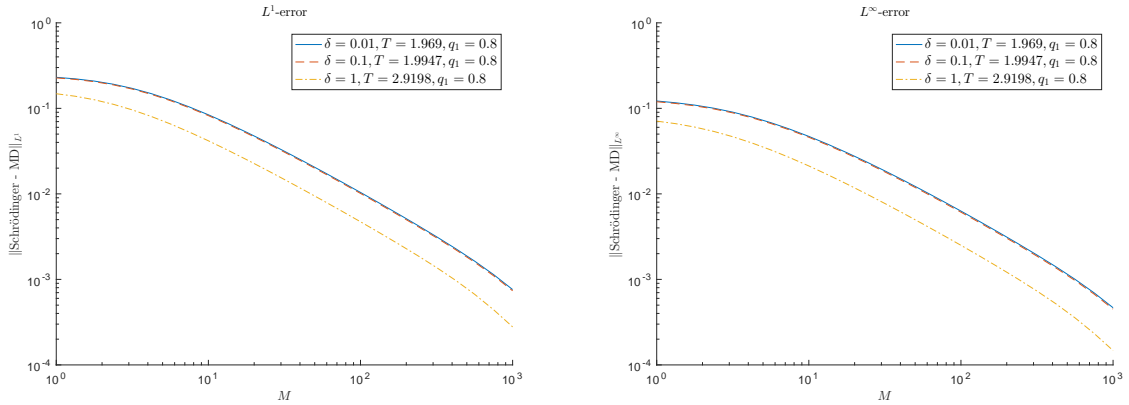
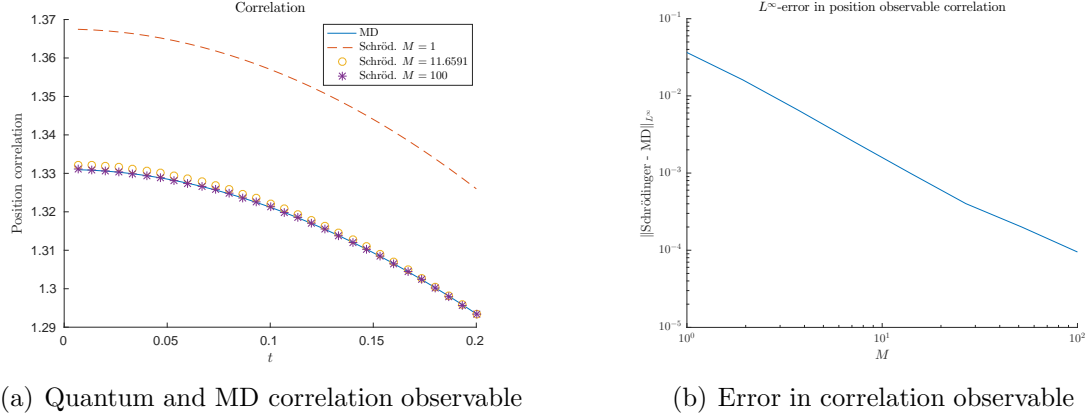


FIGURE 2. The quantities  $\delta$  and  $T$  are chosen so that  $q_1 = 0.8$ . The error in the molecular dynamics density approximation, compared to the Schrödinger density approximation, is inverse proportional to the mass ratio  $M$  for all  $\delta$ .

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(a) Quantum and MD correlation observable

(b) Error in correlation observable

FIGURE 3. (a) Molecular dynamics position observable correlation shown together with the Schrödinger position observable correlation for 3 sample mass ratios. (b) The  $L^\infty$ -error in the molecular dynamics position observable correlation approximation, compared to the Schrödinger position observable correlation approximation, is inverse proportional to the mass ratio  $M$ .

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INSTITUTIONEN FÖR MATEMATIK, KUNGL. TEKNISKA HÖGSKOLAN, 100 44 STOCKHOLM, SWEDEN  
*E-mail address:* `kammo@kth.se`

INSTITUTIONEN FÖR MATEMATIK, KUNGL. TEKNISKA HÖGSKOLAN, 100 44 STOCKHOLM, SWEDEN  
*E-mail address:* `msandb@kth.se`

INSTITUTIONEN FÖR MATEMATIK, KUNGL. TEKNISKA HÖGSKOLAN, 100 44 STOCKHOLM, SWEDEN  
*E-mail address:* `szepepsy@kth.se`